HANDBOOK OF PHYSICAL VAPOR DEPOSITION (PVD) PROCESSING

Film Formation, Adhesion, Surface Preparation and Contamination Control

by

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Society of Vacuum Coaters
Albuquerque, New Mexico

np
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Dedication

To my wife
Vivienne

Without Vivienne's constant support, encouragement, and editorial assistance, this book would not exist. Her wide spectrum of contacts within the vacuum equipment and PVD technology industries has made the accumulation of information in some sections of this book possible.

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Preface

The motivation for writing this book was that there was no single source of information which covers all aspects of Physical Vapor Deposition (PVD) processing in a comprehensive manner. The properties of thin films deposited by PVD processes depend on a number of factors (see Sec. 1.2.2), and each must be considered when developing a reproducible process and obtaining a high product throughput and yield from the production line.

This book covers all aspects of PVD process technology from characterizing and preparing the substrate material, through the deposition process and film characterization, to post deposition processing. The emphasis of the book is on the aspects of the process flow that are critical to reproducible deposition of films that have the desired properties.

The book covers both neglected subjects, such as film adhesion, substrate surface characterization, and the external processing environment, and widely discussed subjects, such as vacuum technology, film properties and the fundamentals of individual deposition processes. In this book, the author relates these subjects to the practical issues that arise in PVD processing, such as contamination control and substrate property effects on film growth, which are often not discussed or even mentioned in the literature. By bringing these subjects together in one book, the author has made it possible for the reader to better understand the interrelationships between various aspects of the processing and the resulting film properties. The author draws upon his long experience in developing PVD processes, teaching short courses on PVD processing, to not only present the basics but

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also to provide useful hints for avoiding problems and solving problems when they arise. Some examples of actual problems and solutions ("war stories") are provided as foot notes throughout the text. The organization of the text allows a reader who is already knowledgeable in the subject to scan through a section and find subjects that are of particular interest. Extensive references allow the reader to pursue subjects in greater detail if so desired.

An important aspect of the book is the useful reference material presented in the Appendices. A glossary of over 2500 terms and acronyms will be especially useful to those individuals that are just entering the field and those who are not fully conversant with the English language. Many of the terms are colloquialisms that are used in the field of Surface Engineering.

The author realizes that covering this subject is a formidable task, particularly for one person, and that this effort is incomplete at best. He would like to elicit comments, corrections, and additions, which may be incorporated in a later edition of the book. In particular, he would like to elicit "war stories" of actual problems and solutions. Credit will be given for those which are used. Please contact the author at (ph.) 505-856-6810, (fax) 505-856-6716, or e-mail donmattox@svc.org.

Albuquerque, New Mexico — Donald M. Mattox
August, 1997

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1

Introduction

1.1 SURFACE ENGINEERING

Surface engineering involves changing the properties of the surface and near-surface region in a desirable way. Surface engineering can involve an overlay process or a surface modification process. In overlay processes a material is added to the surface and the underlying material (substrate) is covered and not detectable on the surface. A surface modification process changes the properties of the surface but the substrate material is still present on the surface. For example, in aluminum anodization, oxygen reacts with the anodic aluminum electrode of an electrolysis cell to produce a thick oxide layer on the aluminum surface. Table 1-1 shows a number of overlay and surface modification processes that can be used for surface engineering.

Each process has its advantages, disadvantages and applications. In some cases surface modification processes can be used to modify the substrate surface prior to depositing a film or coating. For example a steel surface can be hardened by plasma nitriding (ionitriding) prior to the deposition of a hard coating by a PVD process. In other cases, a surface modification process can be used to change the properties of an overlay coating. For example, a sputter-deposited coating on an aircraft turbine blade can be shot peened to densify the coating and place it into compressive stress.

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Table 1-1. Processes for Surface Engineering

Atomistic/Moleular Deposition

Electrolytic Environment
- Electroplating
- Electroless plating
- Displacement plating
- Electrophoretic deposition

Vacuum Environment
- Vacuum evaporation
- Ion beam sputter deposition
- Ion beam assisted deposition (IBAD)
- Laser vaporization
- Hot-wire and low pressure CVD
- Jet vapor deposition
- Ionized cluster beam deposition

Plasma Environment
- Sputter deposition
- Arc vaporization
- Ion Plating
- Plasma enhanced (PE)CVD
- Plasma polymerization

Chemical Vapor Environment
- Chemical vapor deposition (CVD)
- Pack cementation

Chemical Solution
- Spray pyrolysis
- Chemical reduction

Particulate Deposition

Thermal Spray
- Flame Spray
- Arc-wire spray
- Plasma spraying
- D-gun
- High-vel-oxygen-fuel (HVOF)

Impact Plating

Bulk Coatings

Wetting Processes
- Dip coating
- Spin coating
- Painting

Fusion Coatings
- Thick films
- Enameling
- Sol-gel coatings
- Weld overlay

Solid Coating
- Cladding
- Gilding

Surface Modification

Chemical Conversion
- Wet chemical solution (dispersion & layered)
- Gaseous (thermal)
- Plasma (thermal)

Electrolytic Environment
- Anodizing
- Ion substitution

Mechanical
- Shot peening
- Work hardening

Thermal Treatment
- Thermal stressing

Ion Implantation
- Ion beam
- Plasma immersion ion implantation

Roughening and Smoothing
- Chemical
- Mechanical
- Chemical-mechanical polishing
- Sputter texturing

Enrichment and Depletion
- Thermal
- Chemical

An atomistic film deposition process is one in which the overlay material is deposited atom-by-atom. The resulting film can range from single crystal to amorphous, fully dense to less than fully dense, pure to impure, and thin to thick. Generally the term "thin film" is applied to layers which have thicknesses on the order of several microns or less (1 micron = 10^{-6} meters) and may be as thin as a few atomic layers. Often the properties of thin films are affected by the properties of the underlying material (substrate) and can vary through the thickness of the film. Thicker layers are generally called coatings. Atomistic deposition process can be done in a vacuum, plasma, gaseous, or electrolytic environment.

1.1.1 Physical Vapor Deposition (PVD) Processes

Physical Vapor Deposition (PVD) processes (often just called thin film processes) are atomistic deposition processes in which material is vaporized from a solid or liquid source in the form of atoms or molecules, transported in the form of a vapor through a vacuum or low pressure gaseous (or plasma) environment to the substrate where it condenses. Typically, PVD processes are used to deposit films with thicknesses in the range of a few nanometers to thousands of nanometers; however they can also be used to form multilayer coatings, graded composition deposits, very thick deposits and freestanding structures. The substrates can range in size from very small to very large such as the 10' x 12' glass panels used for architectural glass. The substrates can range in shape from flat to complex geometries such as watchbands and tool bits. Typical PVD deposition rates are 10–100Å (1–10 nanometers) per second.

PVD processes can be used to deposit films of elements and alloys as well as compounds using reactive deposition processes. In reactive deposition processes, compounds are formed by the reaction of depositing material with the ambient gas environment such as nitrogen (e.g. titanium nitride, TiN) or with a co-depositing material (e.g. titanium carbide, TiC). Quasi-reactive deposition is the deposition of films of a compound material from a compound source where loss of the more volatile species or less reactive species during the transport and condensation process, is compensated for by having a partial pressure of reactive gas in the deposition environment. For example, the quasi-reactive sputter deposition of ITO (indium-tin-oxide) from an ITO sputtering target using a partial pressure of oxygen in the plasma.

The main categories of PVD processing are vacuum evaporation, sputter deposition, and ion plating as depicted in Fig. 1-1.

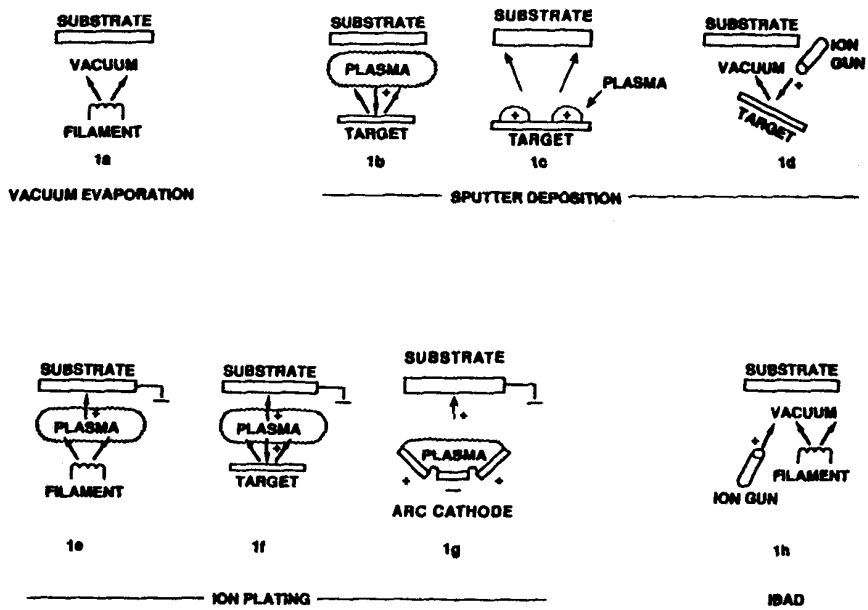


Figure 1-1. PVD processing techniques: (*1a*) vacuum evaporation, (*1b* and *1c*) sputter deposition in a plasma environment, (*1d*) sputter deposition in a vacuum, (*1e*) ion plating in a plasma environment with a thermal evaporation source, (*1f*) ion plating with a sputtering source, (*1g*) ion plating with an arc vaporization source and, (*1h*) Ion Beam Assisted Deposition (IBAD) with a thermal evaporation source and ion bombardment from an ion gun.

Vacuum Deposition

Vacuum deposition (Ch. 5) which is sometimes called vacuum evaporation is a PVD process in which material from a thermal vaporization source reaches the substrate with little or no collision with gas molecules in the space between the source and substrate . The trajectory of the vaporized material is "line-of-sight". The vacuum environment also provides the ability to reduce gaseous contamination in the deposition system to a low level. Typically, vacuum deposition takes place in the gas pressure range of 10^{-5} Torr to 10^{-9} Torr depending on the level of gaseous contamination that can be tolerated in the deposition system. The thermal

vaporization rate can be very high compared to other vaporization methods. The material vaporized from the source has a composition which is in proportion to the relative vapor pressures of the material in the molten source material. Thermal evaporation is generally done using thermally heated sources such as tungsten wire coils or by high energy electron beam heating of the source material itself. Generally the substrates are mounted at an appreciable distance away from the evaporation source to reduce radiant heating of the substrate by the vaporization source.

Vacuum deposition is used to form optical interference coatings, mirror coatings, decorative coatings, permeation barrier films on flexible packaging materials, electrically conducting films, wear resistant coatings, and corrosion protective coatings.

Sputter Deposition

Sputter deposition (Ch. 6) is the deposition of particles vaporized from a surface ("target"), by the physical sputtering process. Physical sputtering is a non-thermal vaporization process where surface atoms are physically ejected from a solid surface by momentum transfer from an atomic-sized energetic bombarding particle which is usually a gaseous ion accelerated from a plasma. This PVD process is sometimes just called sputtering, i.e. "sputtered films of —" which is an improper term in that the film is not being sputtered. Generally the source-to-substrate distance is short compared to vacuum deposition. Sputter deposition can be performed by energetic ion bombardment of a solid surface (sputtering target) in a vacuum using an ion gun or low pressure plasma (<5 mTorr) (Ch. 4) where the sputtered particles suffer few or no gas phase collisions in the space between the target and the substrate. Sputtering can also be done in a higher plasma pressure (5–30 mTorr) where energetic particles sputtered or reflected from the sputtering target are "thermalized" by gas phase collisions before they reach the substrate surface. The plasma used in sputtering can be confined near the sputtering surface or may fill the region between the source and the substrate. The sputtering source can be an element, alloy, mixture, or a compound and the material is vaporized with the bulk composition of the target. The sputtering target provides a long-lived vaporization source that can be mounted so as to vaporize in any direction. Compound materials such as titanium nitride (TiN) and zirconium nitride (ZrN) are commonly reactively sputter deposited by using a reactive

gas in the plasma. The presence of the plasma "activates" the reactive gas ("plasma activation") making it more chemically reactive.

Sputter deposition is widely used to deposit thin film metallization on semiconductor material, coatings on architectural glass, reflective coatings on compact discs, magnetic films, dry film lubricants and decorative coatings.

Arc Vapor Deposition

Arc vapor deposition (Ch. 7) uses a high current, low-voltage arc to vaporize a cathodic electrode (cathodic arc) or anodic electrode (anodic arc) and deposit the vaporized material on a substrate. The vaporized material is highly ionized and usually the substrate is biased so as to accelerate the ions ("film ions") to the substrate surface.

Ion Plating

Ion plating (Ch. 8) which is sometimes called Ion Assisted Deposition (IAD) or Ion Vapor Deposition (IVD) utilizes concurrent or periodic bombardment of the depositing film by atomic-sized energetic particles, to modify and control the properties of the depositing film. In ion plating the energy, flux and mass of the bombarding species along with the ratio of bombarding particles to depositing particles are important processing variables. The depositing material may be vaporized either by evaporation, sputtering, arc erosion or by decomposition of a chemical vapor precursor. The energetic particles used for bombardment are usually ions of an inert or reactive gas, or, in some cases, ions of the condensing film material ("film ions"). Ion plating can be done in a plasma environment where ions for bombardment are extracted from the plasma or it may be done in a vacuum environment where ions for bombardment are formed in a separate "ion gun". The latter ion plating configuration is often called Ion Beam Assisted Deposition (IBAD). By using a reactive gas in the plasma, films of compound materials can be deposited. Ion plating can provide dense coatings at relatively high gas pressures where gas scattering can enhance surface coverage. Ion plating is used to deposit hard coatings of compound materials, adherent metal coatings, optical coatings with high densities, and conformal coatings on complex surfaces.

1.1.2 Non-PVD Thin Film Atomistic Deposition Processes

There are a number of other thin film deposition processes that should be considered for certain applications. For example, a TiN hardcoating can be deposited by PVD or CVD.

Chemical Vapor Deposition (CVD) and PECVD

Thermal Chemical Vapor Deposition (CVD) is the deposition of atoms or molecules by the high temperature reduction or decomposition of a chemical vapor precursor species which contains the material to be deposited.[1]-[3] Reduction is normally accomplished by hydrogen at an elevated temperature. Decomposition is accomplished by thermal activation. The deposited material may react with other gaseous species in the system to give compounds (e.g. oxides, nitrides). CVD processing is generally accompanied by volatile reaction byproducts and unused precursor species. CVD has numerous other names and adjectives associated with it such as Vapor Phase Epitaxy (VPE) when CVD is used to deposit single crystal films, Metalorganic CVD (MOCVD) when the precursor gas is a metalorganic species, Plasma Enhanced CVD (PECVD) when a plasma is used to induce or enhance decomposition and reaction, and Low Pressure CVD (LPCVD) when the pressure is less than ambient.

Plasmas can be used in CVD reactors to "activate" and partially decompose the precursor species. This allows deposition at a temperature lower than thermal CVD and the process is called plasma-enhanced CVD (PECVD) or plasma-assisted CVD (PACVD).[4]-[7] The plasmas are typically generated by radio-frequency (rf) techniques. Figure 1-2 shows a parallel plate CVD reactor that uses radio frequency (rf) power to generate the plasma. This type of PECVD reactor is in common use in the semiconductor industry to deposit silicon nitride (Si_3N_4) and phosphosilicate glass (PSG) encapsulating layers a few microns thick with deposition rates of 5–100 nm/min. At low pressures, concurrent energetic particle bombardment during deposition can affect the properties of films deposited by PECVD.[8]

Plasma-based CVD can also be used to deposit polymer films (plasma polymerization).[9][10] In this case the precursor vapor is a monomer that becomes crosslinked in the plasma and on the surface to form an organic or inorganic polymer film. These films have very low porosity and excellent surface coverage. When plasma depositing films

from organo-silane precursors, oxygen can be added to the plasma to oxidize more or less of the silicon in the film.[11]

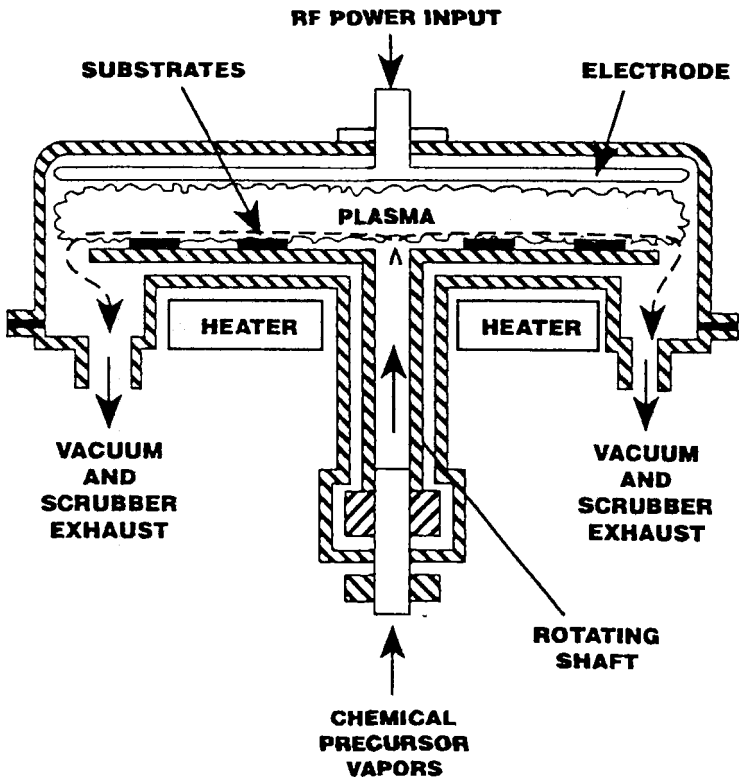


Figure 1-2. Parallel plate PECVD reactor. Typical parameters are: rf frequency—50 kHz to 13.56 MHz; temperature—25 to 700ºC; pressure—100 mTorr to 2 Torr; gas flow rate—200 sccm.

Electroplating, Electroless Plating and Displacement Plating

Electroplating is the deposition on the cathode of metallic ions from the electrolyte of an electrolysis cell.[12]-[15] Only about 10 elements (Cr, Ni, Zn, Sn, In, Ag, Cd, Au, Pb, and Rh) are commercially deposited from aqueous solutions. Some alloy compositions such as Cu-Zn, Cu-Sn, Pb-Sn, Au-Co, Sn-Ni, Ni-Fe, Ni-P and Co-P are commercially deposited.

Conductive oxides such as PbO_2 and Cr_2O_3 can also be deposited by electroplating. A thin film of material deposited by electroplating is often called a "flash" and is on the order of 40 thousandths of an inch thick. Typically, the anode of the electrolytic cell is of the material being deposited and is consumed in the deposition process. In some cases, the anode material is not consumed and the material to be deposited comes only from solution. For example, lead oxide, PbO_2, can be electrodeposited from a lead nitrate plating bath using carbon anodes. Stainless steel and platinum are also often used as non-consumable anode materials.

In electroless or autocatalytic plating no external voltage/current source is required. The voltage/current is supplied by the chemical reduction of an agent at the deposit surface. The reduction reaction is catalyzed by a material, which is often boron or phosphorous. Materials that are commonly deposited by electroless deposition are: Ni, Cu, Au, Pd, Pt, Ag, Co and Ni-Fe alloys. Displacement plating is the deposition of ions in solution on a surface and results from the difference in electronegativity of the surface and the ions. The relative electronegativities of some elements are shown in Table 1-2. For example, gold in solution will displacement plate-out on copper and lead will displacement plate-out on aluminum.

Electrophoresis is the migration of charged particles in an electric field. Electrophoretic deposition, or electrocoating, is the electrodeposition of large charged particles from a solution.[16][17] The particles may be charged dielectric particles (glass particles, organic molecules, paint globules, etc.) which are non-soluble in the aqueous electrolyte. Alternatively some of the components can be treated so they are soluble in water but will chemically react in the vicinity of an electrode so their solubility is decreased. Particles are usually deposited on the anode but sometimes on the cathode (cataphoresis).

Chemical Reduction

Some thin films can be deposited from chemical solutions at low temperatures by immersion in a two-part solution that gives a reduction reaction. "Chemical silvering" of mirrors and vacuum flasks is a common example.[18][19] The glass surface to be silvered is cleaned very thoroughly then nucleated using a hot acidic stannous chloride solution or by vigorous swabbing with a saturated solution of $SnCl_2$. The surface is then immediately immersed in the silvering solution where a catalyzed chemical reduction will cause silver to be deposited on the glass surface. Copper oxide

(Cu_2O) films can be deposited from mixing solutions of $CuSO_4 + Na_2S_2O_3$ (sodium thiosulfate) and NaOH.

Elemental materials such as platinum, gold, tin, indium can be deposited by the thermal decomposition of a chemical solution. For example, platinum can be deposited by the thermal decomposition of platinum chloride in solution.

Table 1-2. Electronegativities

THE ELECTROMOTIVE SERIES

MATERIAL	POTENTIAL (V)	MATERIAL	POTENTIAL (V)
$Li \rightleftharpoons Li^+$	-3.045	$Co \rightleftharpoons Co^{2+}$	-0.277
$Rb \rightleftharpoons Rb^+$	-2.93	$Ni \rightleftharpoons Ni^{2+}$	-0.250
$K \rightleftharpoons K^+$	-2.924	$Sn \rightleftharpoons Sn^{2+}$	-0.136
$Ba \rightleftharpoons Ba^{2+}$	-2.90	$Pb \rightleftharpoons Pb^{2+}$	-0.126
$Sr \rightleftharpoons Sr^{2+}$	-2.90	$Fe \rightleftharpoons Fe^{3+}$	-0.04
$Ca \rightleftharpoons Ca^{2+}$	-2.87	$Pt/H_2 \rightleftharpoons H^+$	0.0000
$Na \rightleftharpoons Na^+$	-2.715	$Sb \rightleftharpoons Sb^{3+}$	+0.15
$Mg \rightleftharpoons Mg^{2+}$	-2.37	$Bi \rightleftharpoons Bi^{3+}$	+0.2
$Al \rightleftharpoons Al^{3+}$	-1.67	$As \rightleftharpoons As^{3+}$	+0.3
$Mn \rightleftharpoons Mn^{2+}$	-1.18	$Cu \rightleftharpoons Cu^{2+}$	+0.34
$Zn \rightleftharpoons Zn^+$	-0.762	$Pt/OH \rightleftharpoons O_2$	+0.40
$Cr \rightleftharpoons Cr^{3+}$	-0.74	$Cu \rightleftharpoons Cu^+$	+0.52
$Cr \rightleftharpoons Cr^{2+}$	-0.56	$Hg \rightleftharpoons Hg^{2+}$	+0.789
$Fe \rightleftharpoons Fe^{2+}$	-0.441	$Ag \rightleftharpoons Ag^+$	+0.799
$Cd \rightleftharpoons Cd^{2+}$	-0.402	$Pd \rightleftharpoons Pd^{2+}$	+0.987
$In \rightleftharpoons In^{3+}$	-0.34	$Au \rightleftharpoons Au^{3+}$	+1.50
$Tl \rightleftharpoons Tl^+$	-0.336	$Au \rightleftharpoons Au^+$	+1.68

1.1.3 Applications of Thin Films

Some of the most utilized applications of thin film deposition processes include:

- Single and multilayer metal electrical conductor films
- Optical films for transmission and reflection
- Decorative films
- Decorative and wear-resistant (decorative/functional) coatings
- Permeation barriers for moisture and gases

- Corrosion resistant films
- Electrically insulating layers for microelectronics
- Coating of engine turbine blades
- Coating of high strength steels to avoid hydrogen embrittlement
- Diffusion barrier layers for semiconductor metallization
- Magnetic films for recording
- Transparent electrical conductors
- Wear and erosion resistant (hard) coatings (tool coatings)
- Dry film lubricants
- Thin-walled freestanding structures

1.2 THIN FILM PROCESSING

1.2.1 Stages of Fabrication

The production of useful and commercially attractive "engineered surfaces" using thin film deposition processes involves a number of stages which are interdependent. The stages are:

- Choice of the substrate ("real surface"—Ch. 2)
- Defining and specifying critical properties of the substrate surface
- Development of an appropriate surface preparation process which includes cleaning and may involve changing the surface morphology or chemistry (surface modification).
- Selection of the film material(s) and film structure to produce the film adhesion and film properties required
- Choice of the fabrication process to provide reproducible film properties and long term stability
- Development of production equipment that will give the necessary product throughput
- Development of the fabrication equipment, process parameters, parameter limits, and monitoring/control techniques to give a good product yield

- Development of appropriate characterization techniques to determine the properties and stability of the product
- Possibly the development of techniques for reprocessing or repair of parts with defective coatings
- Creation of written specifications and manufacturing processing instructions (MPIs) for all stages of the processing

1.2.2 Factors that Affect Film Properties

Deposited thin films and coatings generally have unique properties compared to the material in bulk form and there are no handbook values for film properties. There have been many books and articles on film deposition and film properties but generally these treatments do not emphasize the importance of the substrate surface and deposition conditions on the film properties. The properties of a film of a specific material formed by any atomistic deposition process depends on four factors, namely:

- *Substrate surface condition before and after cleaning and surface modification*—e.g., surface morphology (roughness, inclusions, particulate contamination), surface chemistry (surface composition, contaminants), mechanical properties, surface flaws, outgassing, preferential nucleation sites, and the stability of the surface.
- *Details of the deposition process and system geometry*—e.g., deposition process used, angle-of-incidence distribution of the depositing adatom flux, substrate temperature, deposition rate, gaseous contamination, concurrent energetic particle bombardment (flux, particle mass, energy).
- *Details of film growth on the substrate surface*—e.g., condensation and nucleation of the arriving atoms (adatoms), interface formation, interfacial flaw generation, energy input to the growing film, surface mobility of the depositing adatoms, growth morphology of the film, gas entrapment, reaction with deposition ambient (including reactive deposition processes), changes in the film properties during deposition.
- *Postdeposition processing and reactions*—e.g., chemical reaction of the film surface with the ambient, subsequent

processing, thermal or mechanical cycling, corrosion, interfacial degradation; surface treatments such as burnishing of soft surfaces, shot peening, overcoating ("topcoat"), or chemical modification such as chromate conversion.

In order to have reproducible film properties each of these factors must be reproducible. When problems occur in manufacturing each of these factors should be considered as a possible source of the problem.

Chapter 2 discusses the real surface (substrate) on which the film must be deposited. This real surface never has the same composition as the bulk material. With some materials, such as polymers, the surface and bulk material are affected by its history. Characterization of the elemental, phase, microstructural, morphological and physical properties of real surfaces is important in establishing criteria for the reproducible surface necessary to produce reproducible film properties. The substrate surface morphology can have a large effect on the film morphology and properties as discussed in Ch. 9. The physical and mechanical properties of the substrate surface can affect the performance of the film structure and the apparent adhesion of the film to the surface (Ch. 11). The real surface can be modified in desirable ways prior to the deposition of the film structure.

A contaminant can be defined as any material in the ambient or on the surface that interferes with the film formation process, affects the film properties or influences the film stability in an undesirable way. In most cases the concern is with both the type and amount of the contaminant. Contaminants can cover the whole surface such as oxide reaction layers or an adsorbed hydrocarbon layer or they can be limited to restricted areas such as particulates or fingerprints. A major concern in processing is the variability of the contamination in such a manner as to affect product and process reproducibility. Cleaning is the reduction of the type and amount of contamination to an acceptable level of the substrate surface is an important step in PVD processing and is discussed in Chapter 12. In PVD processing this cleaning can be done external to the deposition system (external cleaning) and internal to the deposition system (in situ cleaning). The manner in which a surface can be cleaned is often controlled, to some extent, by government regulations on pollution control (US-EPA) and workplace safety (US-OSHA).

Contamination encountered in PVD processes can be categorized as:

- *Substrate surface related*—e.g. oxide layers on metals, embedded particulates

- *Ambient (external) process related*—e.g. chemical residues, water stains
- *Ambient (external) environment-related*—e.g. settled airborne particulates, adsorbed water vapor and hydrocarbons
- *Deposition environment related*—e.g. residual gases in vacuum/plasma environment, water desorbed from vacuum surfaces, particulates and vapors in the deposition system
- *Deposition process related*—e.g. contaminant vapors and particulates from vaporization sources, fixtures and tooling
- *Postdeposition contamination*—e.g. oxides formed on the free surfaces of the deposited film, adsorbed hydrocarbons

Chapters 3 and 4 discuss the environment in the deposition chamber and how this environment can contribute to contamination that affects film properties. The properties of the deposition environment are determined by contamination in the vacuum or plasma environment and contamination released by the processing. Often these sources of contamination can change with time due to changes in the internal surface area of the deposition system as film material builds up on fixtures and vacuum surfaces, degradation of the vacuum integrity of the system, degradation of the vacuum pumping system, build-up of contamination from all sources, catastrophic changes due to a lack of fail-safe design of the deposition system and/or improper operating procedures. These changes can be reflected in product yield. Where very clean processing is required, such as used in the semiconductor industry, contamination in the deposition ambient can be the controlling factor in product yield.

Chapter 13 discusses the external processing environment which is the laboratory or production environment in which the substrates, fixtures, vaporization sources, etc. are processed prior to insertion in the deposition chamber. This environment consists not only of the air but also processing gas and fluids, surfaces which can come into contact with the substrate, etc. This processing environment always contains potential contaminants. The control of this environment is often critical to insuring process and product reproducibility. In some cases, the effect of the processing environment can be minimized by integrating the external processing into the processing line. An example is the use of washing and drying modules connected to the in-line deposition system used to coat flat-glass mirrors.

1.2.3 Scale-Up and Manufacturabilty

The ability to scale-up a deposition process and associated equipment to provide a quality product at an attractive price is essential in commercialization of any process. It is important that the development work be done on representative substrate material and with processes and equipment that can be scaled to production requirements.*,** An important factor in manufacturability is the deposition fixturing which holds the substrates in the deposition chamber. The fixturing determines how the parts are held and moved and the number of parts that can be processed in each cycle. The vacuum pumping system and deposition chamber size are also important in determining the process cycle-time.

In order to design an appropriate vacuum system for a PVD process, it is necessary to determine the additional pumping load that will be added during the processing cycle. This can only be determined after the fixturing design has been selected and the number of parts to be processed at one time has been determined. For example, the metallization of compact discs (CDs) with aluminum was originally done in a batch process where hundreds of molded discs were coated in one run in a large vacuum vessel with several hours cycle time. Now the CDs are coated one-at-a-time with a cycle time of less than 3 seconds. This was accomplished by integrating the molding equipment and the deposition equipment so that

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*A prominant R&D laboratory developed a solar-thermal absorbing coating which involved the Chemical Vapor Deposition (CVD) of a dendritic tungsten coating. The coating worked very well and was awarded an IR 100 award. The problem was that the process could not be economically scaled-up to the thousands of square meters per year required for commercialization of the product, so it has never been used.

**In the mid-sixties several steel manufacturers wanted to use PVD deposited aluminum to replace hot dipped galvanized steel for coating steel strips. The researchers in the laboratory took carefully prepared steel surfaces and showed that corrosion-resistant aluminum coatings could be deposited. Many millions of dollars were invested in plants to coat mill-roll steel. It was found that the coated mill-rolled steel developed pinhole-corrosion in service and the cause was traced to inclusions rolled into the steel surface during fabrication. There was no good technique for cleaning the surface and the project failed with the loss of many millions of dollars. The problem was that the process development was done on non-representative material with unrealistic substrate surface preparation techniques.

the discs were not exposed to the air between processes and outgassing problems are avoided.

Often a concern in coating technology is repair and rework. Repair and rework may mean reprocessing small areas of coating. This is often difficult and the parts are often stripped and reprocessed. Repair and rework is often more difficult and expensive for PVD processing than for other coating techniques such as electroplating or painting.

1.3 PROCESS DOCUMENTATION

The key to reproducible processing is documentation. Documentation is also important in the transfer of a process or product from research and development to manufacturing (Appendix 2), in improving the process over time, and to qualify for the ISO 9000 certifications. There have been many instances where the lack of proper documentation has resulted in the loss of product yield and even in the loss of the process itself. Documentation should cover the whole process flow. Often some stages of the processing, such as cleaning and film deposition, are well covered but some intermediate stages, such as handling and storage, are not. It is often helpful to generate a process flow diagram that covers the processing, handling and storage from the as-received material through the packaged product as shown in Fig. 1-3. Documentation associated with each stage can be indicated on the diagram.

1.3.1 Process Specifications

Process specifications ("specs") are essentially the "recipe" for the process and are the goal of a focused R&D process or product development effort. Specifications define what is done, the critical process parameters and the process parameter limits that will produce the desired product. The specification can also define the substrate material, materials to be used in the processing, handling and storage conditions; packaging, process monitoring and control techniques, inspection, testing, safety considerations, and any other aspect of the processing that is of importance. Specifications should be dated and there should be a procedure available that allows changes to the specifications. Reference should be made to the particular "issue" (date) of specifications. Specifications should be based

on accurate measurements so it is important that calibrated instrumentation be used to establish the parameter limits (parameter windows) for the process. Specifications usually do not necessarily specify specific equipment and non-critical process parameters. Specifications are also used to define the properties of the substrate surface, the functional and stability properties of the product, and associated test methods.

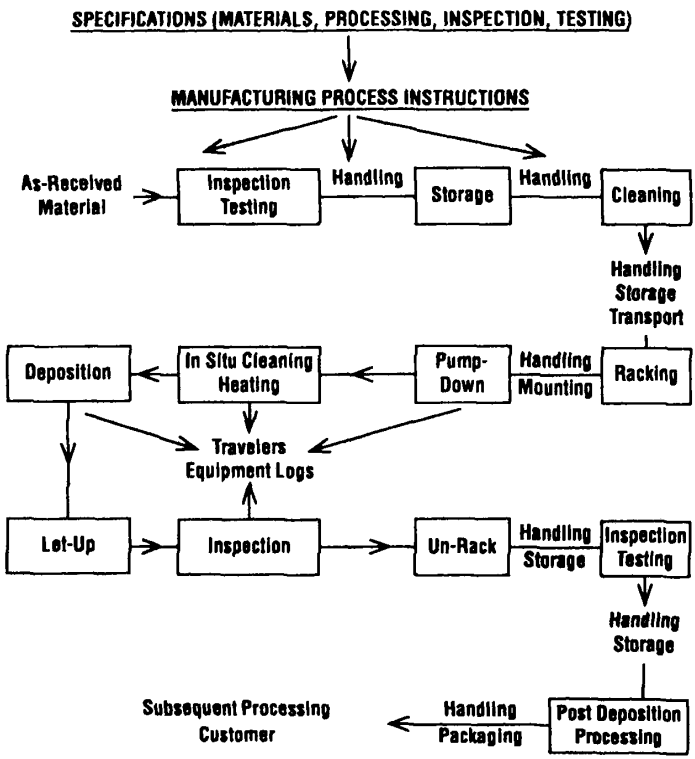


Figure 1-3. Processing flow chart.

Generation of the specification entails a great deal of careful effort so as to not miss a critical detail and to allow as large a processing parameter window as is possible (i.e., a "robust" process). Factorial design of experiments is used to generate the maximum amount of information

from the least number of experiments.[20] Writing specifications begin with the Laboratory/Engineering (L/E) notebooks from which the critical process parameters and parameter windows are extracted. In many cases, as the specifications are being written it will be necessary to expand the development work to further define critical processes and their parameter windows. Sometimes critical details on the processing are not to be found in the L/E Notebooks but are given by the person performing the work or noted by a trained observer who watches what is being done.

Laboratory/Engineering Notebook

Documentation starts with the Laboratory/Engineering (L/E) Notebook where the experiments, trials and results of experiments, and development work are documented. Where the data is not amenable to direct entry, a summary of the findings can be entered into the L/E notebook and reference made to particular charts, graphs, memos, etc. To ensure unquestionable entries, the L/E notebook should be hardbound, have numbered pages, and entries should be handwritten, dated, and initialed. If an entry is made about a patentable process, product or idea, the entry should be read by another person then, initialed and dated with the statement "read and understood" by the entry.[21] Patents are developed from L/E notebooks and dated entries will be important if questions are ever raised about when and where an idea was conceived or a finding made. Some companies require two L/E notebooks. One for laboratory use, and one that is continuously updated and kept in a fireproof safe.

1.3.2 Manufacturing Process Instructions (MPIs)

Manufacturing Processing Instructions (MPIs) are derived from the specifications as they are applied to specific equipment and manufacturing procedures. A series of MPIs should exist for the complete process flow. MPIs are written by taking the relevant specifications and breaking them down into tasks and subtasks (e.g., cleaning—UV/Ozone) for the operator to follow and can change as the manufacturing maturity develops. Often the MPIs contain information that is not found in the specifications but is important to the manufacturing flow. This may be something such as the type of gloves to be used with specific chemicals (e.g., no vinyl gloves around isopropyl alcohol, rubber gloves for acids). The MPIs should be

dated and updated in a controlled manner. The MPIs should also include the appropriate Manufacturing Safety Data Sheets (MSDSs) for the materials being used. In many cases the MPIs should be reviewed with the R&D staff who have been involved in writing the specifications to ensure that mistakes are not made. The R&D staff should be included in Process Review meetings for the same reason. In some cases MPIs and specifications must be written from an existing process. Care must be taken that the operators reveal all of the important steps and parameters.

1.3.3 Travelers

In some cases the substrates and product may be in a common group or "lot" which can be identified. In this case it may be desirable to have a "Traveler" which accompanies the group of substrates through the processing flow and contains information on which specifications and MPIs were used and the observations made by the operators. The Traveler can include the Process Sheet that details the process parameters used for each deposition ("run"). The travelers can then become the archival records for that particular group of product. It may be desirable to retain archival samples of the product with appropriate documentation. This procedure will assist in failure analysis if there is a problem with the product either during subsequent processing or in service. These samples can be prepared periodically or when there have been significant changes in the process(es) being used. The travelers should be "human engineered" so that the operator has to pay attention to the process and not just push a button.*

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*The blown fuse. In production, a high voltage component was coated with a conformal organic coating and then potted in an organic encapsulant. To ensure good adhesion and high voltage breakdown strength between the coating and the encapsulant, the polymer coating was plasma treated. The time between encapsulation and high voltage testing was three months. After high voltage breakdown failures were noted, the process was examined to determine what had caused the problem. When interviewing the operator of the plasma treatment machine, it was stated by the operator that her job was to put the parts in the plasma treatment machine, push the button and take them out. Several months prior to the discovery of the problem, the operator had observed that a meter had stopped giving a reading, but the observation had not been mentioned to anyone. Further investigation discovered that a fuse had blown and the plasma never came on in the machine—3 months of production had to be scrapped. Note that the operator was performing as instructed and nothing else—a good operator with inadequate training.

1.3.4 Equipment and Calibration Logs

In manufacturing, it is important to keep Equipment Logs for the equipment and instrumentation being used. These logs contain information as to when and how long the equipment was used, its performance, any modifications that are made, and any maintenance and service that has been performed. For example, for a vacuum deposition system, the log should include entries on performance such as:

- Date and operators name
- Time to crossover pressure (roughing to high vacuum pumping)
- Time to the base pressure specified
- Leak-up rate between specified pressure levels
- Process being performed
- Chamber pressure during processing
- Fixturing used
- Number and type of substrates being processed
- Mass spectrometer trace at base pressure and during processing
- Total run time

The Equipment Logs can be used to establish routine maintenance schedules and determine the Cost of Ownership (COO) of that particular equipment. When the equipment is being repaired or serviced it is important to log the date, action, and person doing the work. The Equipment Log should also contain the Calibration Log(s) for associated instrumentation.

1.3.5 Commercial/Military Standards and Specifications

Standards are accepted specifications that are issued by various organizations after extensive trials and evaluations. "Recommended practices" are issued where the "practices" have not been as rigorously tested and reviewed as the Standards, but they are generally used in the same manner as Standards. Standards or Specifications may be included in specifications by name (e.g. "as per Mil Spec xx") giving specs within

specs. Some of the organizations which develop industrial specifications and standards related to the vacuum and thin film industry are:

US Military—Military Standards and Specifications (Mil Specs)—available from Document Center, 1504 Industrial Way, Unit 9, Belmont, CA 94002 (www.doccenter.com)

ASTM—American Society for Testing and Materials, 100 Barr Harbor Dr., West Conshohocken, PA 19428 (www.astm.org)

SEMI—Semiconductor Equipment and Materials International, 805 East Middlefield Road, Mountain View, CA 94043-4080 (www.semi.org)

ANSI—American National Standards Institute, 11 West 42nd Street, 13th Floor, New York, NY 10036

NIST—National Institute of Standards and Technology (previously National Bureau of Standards—NBS), Gaithersburg, MD 20899 (www.nist.gov)

ISO—International Standards Organization/Technical Committee 112 for Vacuum Technology—available through ANSI (refer to ASTM Committee E42.94— the ANSI Technical Advisory Group to ISO) (www.ansi.org)

IES—Institute of Environmental Sciences, 940 E Northwest Hwy, Mt. Prospect, Il 60056 (www.isten.vsci.org)

Catalogs and copies of their specifications and standards are available from the various organizations. American Electroplaters and Surface Finishers Society (AESF) plans to have many of the standards from various organization available for sale over the Internet or by mail in 1997.[22] Copies of patents are available from the US Patent Office and commercial search firms. Many government publications and publications on government-sponsored work are available from the National Technical Information Service (NTIS) (703/487-4650, www.ntis.gov) and the Defense Technical Information Center (DTIC), (www.dtic.dla.mil).

1.4 SAFETY AND ENVIRONMENTAL CONCERNS

Safety and environmental concerns are areas where there is a great deal of difference between the development and manufacturing environment. This may be due to the types or amounts of materials used. For example, in the laboratory, a common drying agent is anhydrous alcohol which can be used safely in a well ventilated open area by careful people. However, in manufacturing, fire regulations do not allow alcohol to be used in the open environment because of its low flash point. Instead, the alcohol vapor must be contained and condensed or some other drying technique must be used.

By U.S. law, every worker must be informed about the potential dangers of the chemicals that they encounter in the workplace (OSHA—*Hazard Communication Standard 29 CFR 1910.1200*). This includes common chemicals, such as household dishwasher soaps. It is the responsibility of managers to keep workers informed about the chemicals being used and their potential hazards. Chemical manufacturers must provide users with Manufacturers Safety Data Sheets (MSDSs) on all their chemicals. These MSDSs must be made available to all workers. There are MSDSs on all kinds of chemicals, ranging from the toner used in copiers, to common household detergents, to really hazardous chemicals. Information on environmental aspects of processing can be obtained from the Center for Environmental Research Information.

1.5 UNITS

Throughout the text, units are mixed. This is unconventional, but individuals in the United States must deal with people who know nothing about some of the units used by scientists and engineers. Most individuals have to work and learn in several systems of units. For example, in Europe most vacuum gauges are calibrated in millibars (mbars) while in the United States they are often calibrated in microns or mTorr. Equipment bought from the Europeans will have mbar calibration. When discussing a process, make sure you know what units are being used. If temperatures are given in degrees Fahrenheit (^{o}F) and you think they are in degrees centigrade (^{o}C) some serious misunderstandings can arise.

1.5.1 Temperature Scales

The Centigrade (Celsius) temperature scale (^oC) is based on water freezing at 0^oC and boiling at 100^oC at standard atmospheric pressure (760 Torr). The Fahrenheit temperature scale (^oF) is based on water freezing at 32^oF and boiling at 212^oF at standard atmospheric pressure.

The Kelvin temperature scale (K) is based on zero being the temperature at which all molecular motion ceases and there is no thermal energy present. The Kelvin temperature scale uses 100 K as the temperature difference between the freezing and boiling point of water under standard pressure conditions. Zero degrees Kelvin (0 K) equals -273.16^oC and -459.69^oF.

Note: Conversion: Degrees K = (^oC + 273.16); ^oF = [(9/5 x ^oC) + 32]

1.5.2 Energy Units

Throughout the book the energy of particles will be given in temperature and in electron volts (eV). An electron volt is the energy acquired by a singly charged particle accelerated through a one volt electrical potential. The energy is related to the temperature by the Boltzmann equation given by E = 3/2 kT where k is the Boltzmann constant and T is the Kelvin temperature. One eV is equivalent to about 11,300^oC. In chemical terms 1 eV per atom is equivalent to 23 kilocalories per mole.

1.5.3 Prefixes

Some prefixes adopted by the Système International d'Unités (SI) committee are:[23]

Factor	Prefix	Symbol	Factor	Prefix	Symbol
10^{12}	tera	T	10^{-1}	deci	d
10^{9}	giga	G	10^{-2}	centi	c
10^{6}	mega	M	10^{-3}	mili	m
10^{3}	kilo	k	10^{-6}	micro	μ
10^{2}	hecto	h	10^{-9}	nano	n
10^{1}	deka	da	10^{-12}	pico	p

1.5.4 Greek Alphabet

Greek letters are often used in the text they are as follows (upper case and lower case):

A (α) alpha	Θ (θ) theta	O (ο) omicron	X (χ) chi
B (β) beta	I (ι) iota	Π (π) pi	Ψ (ψ) psi
Γ (γ) gamma	K (κ) kappa	P (ρ) rho	Ω (ω) omega
Δ (δ) delta	Λ (λ) lambda	Σ (σ) sigma	
E (ε) epsilon	M (μ) mu	T (τ) tau	
Z (ζ) zeta	N (ν) nu	Υ (υ) upsilon	
H (η) eta	Ξ (ξ) xi	Φ (φ) phi	

1.6 SUMMARY

Physical Vapor deposition processes are only one set of processes available for surface engineering. In order to make the best choice for obtaining the surface properties desired, all of the possible techniques should be considered.

To stay current with PVD technology one should, as a minimum, have access to the following publications (Appendix 1).

- *Journal of Vacuum Science and Technology A & B* (American Vacuum Society)
- *Proceedings of the Annual Technical Conference of the Society of Vacuum Coaters*
- *Surface and Coating Technology* (Elsevier)
- *Solid State Technology* (PennWell Publications)
- *Precision Cleaning* (Witter Publications)

Useful references are:

- *Surface Engineering*, ASM Handbook, Vol. 5, ASM Publications (1994)
- *Materials Characterization*, ASM Metals Handbook, Vol. 10, 9th edition (1986)

- Pulker, H. K., *Coatings on Glass*, Thin Films Science and Technology Series, No. 6, Elsevier, (under revision) (1984)
- *Handbook of Thin Film Process Technology*, (D. B. Glocker and S. I. Shah, eds.), Institute of Physics Publishing, including supplements (1995)
- *Handbook of Plasma Processing Technology*, (S. M. Rossnagel, J. J. Cuomo, and W. D. Westwood, eds.), Noyes Publications (1990)
- Hablanian, M., *High-Vacuum Technology A Practical Guide*, 2nd edition, Marcel Dekker (1997)
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Handbook of Deposition Technologies for Films and Coating, 2nd edition, (R. Bunshah, ed.), Noyes Publications (1994)

Handbook of Thin Film Technology, (L. I. Maissel and R. Glang, eds.), McGraw-Hill (1970)

Physics of Thin Films (series) Vols. 1-19, edited by several persons, the latest being M. Francombe, and J. L. Vossen, Academic Press (1963–1995)

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2

Substrate ("Real") Surfaces and Surface Modification

2.1 INTRODUCTION

In order to have a reproducible PVD process and product it is necessary to have a reproducible substrate surface. The term "technological surface" can be applied to the "real surface" of engineering materials. These are the surfaces on which films and coatings must be formed. Invariably the real surface differs chemically from the bulk material by having surface layers of reacted and adsorbed material such as oxides and hydrocarbons. These layers, along with the nearby underlying bulk material (near-surface region), comprise the real surface which must be altered to produce the desired surface properties. In some cases the surface must be cleaned and in others the surface may be modified by chemical, mechanical, thermal or other means, to give a more desirable surface by surface modification techniques.

The surface chemistry, morphology and mechanical properties may be important to the adhesion, film formation process and the resulting film properties. The underlying bulk material can be important to the performance of the surface. For example, a hard coating on a soft substrate may not function well, if under load, it is fractured by the deformation of the underlying substrate. The bulk material can also

ClearCorrect Exhibit 1046, Page 54 of 943

influence the surface preparation and the deposition process by the continual outgassing and outdiffusion of internal constituents.

The properties of a surface can be influenced and controlled by the nature of the fabrication of the surface. For example, when machining brittle surfaces such as ceramics, glasses, or carbon, the machining can introduce surface flaws. When the film is deposited on this surface these flaws will be in the interface and when mechanical stress is applied they can easily propagate giving poor adhesion. These surface flaws should be eliminated by chemical etching before the film is deposited. In the machining of metals, if the machining results in deformation of the surface region, a rough surface can be generated and machining lubricants can be folded into the surface. To avoid this, the depth of cut of the final machining should be controlled.

The homogeneity of the surface chemistry and morphology is important to the homogeneity of the deposited film. If the surface is inhomogeneous then the film properties will probably be inhomogeneous. One of the objects of the cleaning and surface modification of substrates is to obtain a homogeneous surface for nucleation and growth of the depositing atoms.

The material can also be controlled by its history. For example, exposure of polymer surfaces to water vapor allows them to absorb water which then outgas during surface preparation and deposition processing. Controlling the history of the material after fabrication can often reduce the variability of the properties of the surface of the material being processed.

Reproducible surfaces are obtained by having reproducible bulk material, reproducible fabrication processes, and reproducible handling and storage techniques. Generally reproducible surfaces for film deposition are obtained by having the appropriate specifications for the purchase, fabrication, surface preparation, handling, storage, and packaging of the substrate material. Techniques should be developed to characterize the surface for critical properties, such as roughness, before the film is deposited. This characterization can be done on the as-received material, after surface modification processing and/or after cleaning of the surface.

2.2 MATERIALS AND FABRICATION

2.2.1 Metals

Metals are solids that have metallic chemical bonding where the atoms are bonded by the "sea" of electrons. Typically metals are ductile,

have some degree of fracture toughness, and have appreciable electrical conductivity. Gold is the only metal that does not form a natural oxide so metals are usually covered with an oxide layer which is the natural or real surface of the material.[1] In some cases the oxide layer is removed from the metal before film deposition takes place but in many cases the film is deposited on the oxide surface. Metal oxides have a high surface energy so a clean metal oxide will absorb low-energy absorbates, such as hydrocarbons, in order to lower its surface energy. These absorbates are the contaminants that must be removed before film deposition.

Metals are often fabricated into shapes by cutting or deformation. The cutting may be by machining, sawing, or shearing. In many cases, the cutting is associated with a lubricant, some of which may remain on the surface as a contaminant. Deformation processing of metals can be in the form of rolling, drawing, or shear forming. These processes can also use lubricants that can become incorporated in the surface and even below the surface. Rolling and shear forming can mechanically impress solid particulates into the surface where they become inclusions in the surface. Deformation often workhardens the surface, making it more resistant to deformation than the bulk of the material. Figure 2-1 depicts a typical surface of a deformed metal surface.

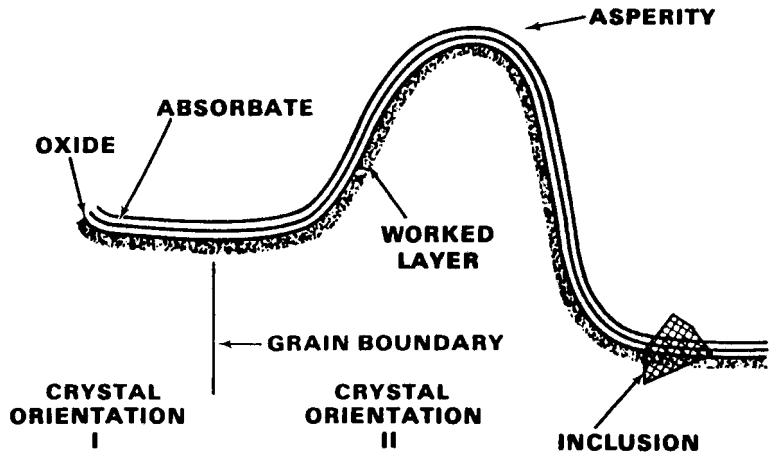


Figure 2-1. Surface of a deformed metal.

Often after fabrication, metal surfaces are protected by oils or a rust preventative to minimize the reaction of the surface with the environment. For example, an oxide-free tool steel surface will form "flash rust" immediately on exposure to the atmosphere. To prevent the flash rust a "flash rust inhibitor" is absorbed on the surface before the cleaned surface is allowed to dry. These additives can act as contaminants in further processing and often are removed by *in situ* cleaning in the deposition system.

Some metal oxides such as chromium oxide (Cr_2O_3), lead oxide (PbO), indium oxide (InO_2), tin oxide (SnO_2), copper oxides (CuO and Cu_2O), and ruthenium oxide (RuO) are electrically conductive but most metal oxides are electrical insulators. The conductive oxides along with conductive nitrides, silicides, and borides are used for diffusion barriers in thin film metallization systems. Often when forming an oxide there is a volume change which introduces stress into the oxide. This stress causes the oxide to spall and the oxidation is progressive and, for iron alloys, is called rust. If the oxide is coherent and has a low stress, it can act to protect the surface from further oxidation (passivation).

Mixtures of metals where there is solid solubility are called alloys. In many cases, the chemical composition of the surface of an alloy differs from that of the bulk composition. For example, the surface of stainless steel, which is an alloy of iron, nickel, and chromium is enriched in chromium which reacts to form a coherent and passive chromium oxide that provides corrosion resistance to the alloy.

Metals can react with each other to form compounds (intermetallic compounds) which have a high degree of ionic chemical bonding. Aluminum is an amphoteric metal which can form intermetallic compounds with other metals either by giving up or accepting an electron. Intermetallic compounds can play an important role in the galvanic corrosion of surfaces, interfaces and films when they are present. For example, Al_2Cu inclusions in an aluminum metallization can cause galvanic corrosion and pitting during the photolithographic process where an electrolyte is in contact with the surface of the metallization. Some intermetallic compounds are electrically conductive, chemically stable ("superstable"), and exceptionally hard. Examples are: Mo_5Ru_3 and W_3Ru_2[2] and $ZrPt_3$ and $ZrIr_3$.[3][4]

2.2.2 Ceramics and Glasses

Ceramics and glasses are generally multicomponent solids that are chemically bonded by ionic or covalent bonding such that there are no free

electrons. Therefore the electrical conductivity and the thermal conductivity is low and the material is brittle. If there is crystallinity the material is called a ceramic and if there is no crystallinity (i.e. amorphous) the material is called a glass. Ceramics and glasses are characterized by a low ductility and low fracture toughness. Some elemental materials such as boron, carbon and silicon, can be formed as an amorphous material, so the definitions must be taken with some exceptions.

Glass substrates are often formed by melting and forming.[5] They can then be molded, flowed, extruded or blown into a fabricated shape. Examples are optical fibers that are extruded through a die, "float glass" which in poured onto the surface of molten tin where it solidifies into the common window glass and glass bottles which are blow-molded. Glasses are also formed by grinding, polishing, and sawing. On heating some glasses in air, mobile species (sodium) will segregate to the surface and form nodules which, if not removed, can cause pinholes in the deposited film.

The composition of glass surfaces can vary with manufacturing conditions and history.[6] Glass surfaces will react with water vapor to hydrate the near-surface region. "Old glass" will have a greater depth of reaction than a fresh surface and the depth of hydration has been used to "date" glass surfaces. Old glass fractures differently than freshly-formed glass because of the hydrated layer. Water will also leach alkali metal ions and silicates from the glass surface.

Float glass is the most common glass that is metallized by PVD processes. The side of the float glass that has been in contact with the molten tin has a tin oxide coating unless it has been chemically removed. The coating appears as a white haze and fluoresces under UV light. The tin oxide can be removed by a light etch with ammonium bifluoride. The packaging of glass can contribute to the contamination to be found on the glass surface.[7]

Glass can be strengthened by placing the surface into compression, producing stressed glass. This makes propagation of surface flaws difficult. The stress and stress profile can be measured by etching the surface and directly measuring the elongation of the material as the compressive stress is removed.

Materials which have a high modulus, a low thermal conductivity and a non-zero coefficient of thermal expansion, such as many glasses, can be strengthened by heating the part then rapidly cooling the surface while the interior cools slowly. This places the surface region in a compressive stress and the interior in a tensile stress state. The material then resists

fracture but if the compressively stressed surface region is fractured, the energy released results in the material fracturing into small pieces. Some glasses can be strengthened by the chemical substitution of large ions for small ions in the surface of the glass using a molten salt bath at high temperatures (chemical strengthening).[8][9] The diffusion process can be aided by the application of an electric field.[10] Some glasses contain nucleating agents that allow the material to be formed as a glass then heat treatment allows crystalliztion so the glass becomes a crystalline ceramic (ceramming glasses).

Ceramics are most often formed by sintering. In sintering, particles in contact at a high temperature become bonded together by the surface diffusion of material in such a manner that the contact points are glued together. Sintered ceramics often are porous. However, under the proper conditions many materials can be made nearly fully dense by sintering.

Ceramic particles can be formed into a solid by having a molten phase that helps cement the particles together. Figure 2-2 shows the surface of a sintered 96% alumina ceramic that is commonly used in microelectronics. This "sintered" material was formed by mixing alumina particles (the "boulders") (96%), with glass particles (4%) and then adding a hydrocarbon binder. The mixture is then formed into a sheet ("slip cast"), heated slowly to burn-off the binder, then heated to a high enough temperature to melt the glass phase which flows over the alumina particles and collects at the particle contacts cementing the particles together. Since the glass has a lower surface energy than the crystalline alumina, each alumina particle has a very thin layer of glass on its surface. Ceramics can also be formed by grinding and polishing, sawing, and chemical vapor deposition (CVD) processes.

Semiconductor materials are special cases of ceramics. Single crystal silicon, for instance, is grown from a melt. To fabricate the silicon substrate material, the bulk material is sliced with a diamond-saw and then polished into "wafers" which can be over eight inches in diameter and as thin as 0.5 micron.

2.2.3 Polymers

A polymer is a large molecule formed by bonding numerous small molecular units, called monomers, together. The most common polymers are the organic polymers, which are based on carbon-hydrogen units which may or may not contain other elements such as nitrogen, oxygen, metals,

etc. Polymers can also be formed from other monomer units such as silicon-hydrogen, boron-hydrogen etc. In building a polymer, many bonds are formed which have various strengths, bond orientations, and separations (bond lengths) between atoms and functional groups. These bonds and the associated chemical environment determine the infrared adsorption and photoelectron emission characteristics of the material.

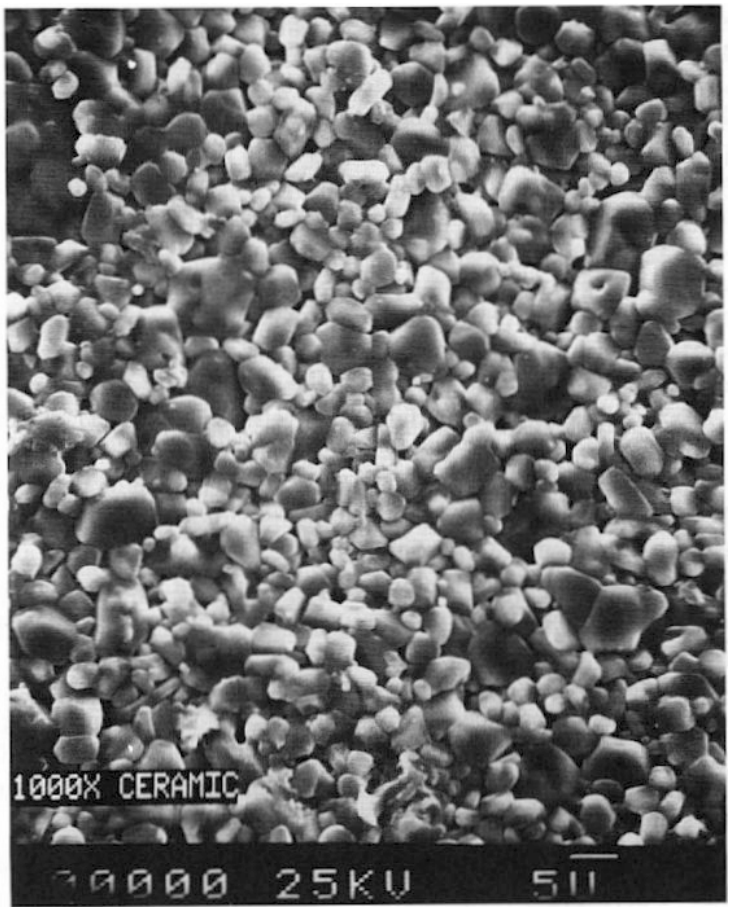


Figure 2-2. Surface of sintered 96% slip cast alumina.

The chemical properties of the polymer surface will depend on the functional groups present on the surface and may depend on the vapor contacting the surface.[11][12] For example, the surface may be different if

the surface has been in an inert atmosphere (argon, nitrogen) or in a water vapor-containing atmosphere. The mechanical properties of the surface region will depend on the amount and type of crosslinking of the polymer material. Often the near-surface region of a polymer material has quite different mechanical properties from the bulk of the material.

2.3 ATOMIC STRUCTURE AND ATOM-PARTICLE INTERACTIONS

2.3.1 Atomic Structure and Nomenclature

An atom is the most fundamental unit of matter that can be associated with a particular element by its atomic structure. The atom consists of a nucleus containing protons (positive charge) and neutrons (neutral charge) in nearly equal numbers. The total mass of the atoms is the sum of the masses and is given in atomic mass units (amu)* or the "Z" of the material. Isotopes of an element have different masses due to differing numbers of neutrons in the nucleus. For example, hydrogen can be H^1 (1 proton) or H^2 (deuterium—1 proton and 1 neutron) or H^3 (tritium—1 proton and 2 neutrons). Surrounding the nucleus are electrons in specific energy ranges called shells or orbitals. The shells are indicated with the letters K, L, M, N as measured from the nucleus outward. The shells are subdivided into several energy levels (s,p,d,—). The inner-shells are filled to the specific number of electrons they can contain (2, 8, 18..). For an uncharged atom there are as many electrons as there are protons. The innermost or core levels are generally full of electrons. The outermost or valence shell can be full or not, depending on the number of electrons available. The shells just below the valence level may not be full. If the outermost shell is full, the atom is called inert since it does not want to bond to other atoms by donating, accepting or sharing an electron. Figure 2-3 shows the atomic structure of copper.

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* The atomic mass unit (amu) is defined as 1/12 of the mass of C^{12} or 1.66×10^{-24} g.

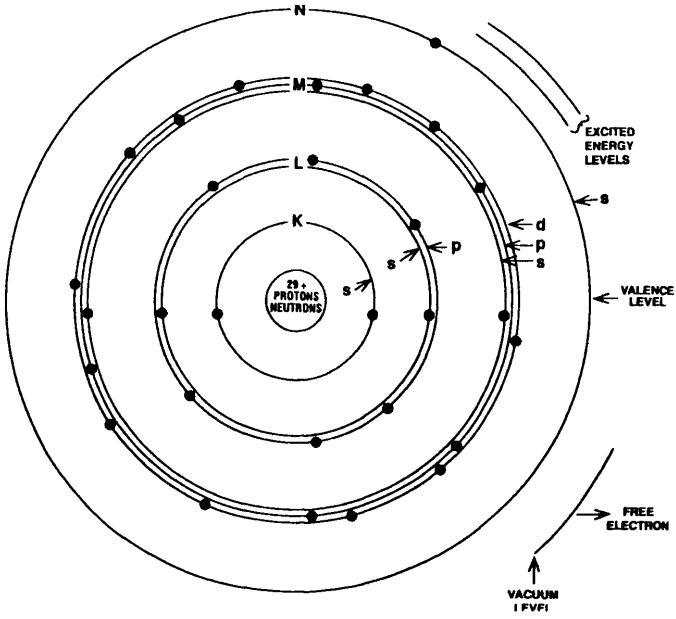


Figure 2-3. Atomic structure of copper.

2.3.2 Excitation and Atomic Transitions

There are energy levels outside the valence shell to which electrons can be excited. Electrons that are excited to these levels will usually return to the lower energy state rapidly with the release of energy in the form of a photon of a specific energy giving rise to an emission spectrum such as the yellow light seen from a sodium vapor lamp. Electrons can remain in certain excited energy levels, called metastable states until they collide with another atom or a surface. Electrons can be excited to such an extent that they leave the atom (vacuum level) and the atom becomes a positive ion. If the atom loses more than one electron it is multiply charged. Atoms can also accept an extra electron and become a negative ion. Atomic electrons can be excited thermally, by an energetic photon, by a colliding with an ion or by a colliding with an electron.

The most common way of exciting or ionizing an atom is by electron-atom collision. Figure 2-4 shows what happens when an energetic electron collides with an atom. The collision can scatter the impinging electron, can excite atomic shell electrons to cause ionization, excite an electron to an excited energy level or backscatter the impinging electron with a loss of energy. When an electron is excited from its energy shell it leaves behind a vacancy. This vacancy can be filled by an electron from another shell which has less binding energy. The energy released by this transition appears as an X-ray having a characteristic energy or by a radiationless process called an Auger transition which provides an Auger electron having a characteristic energy called an Auger electron. This Auger electron will have energies of a few tens to a few thousand electron volts depending on the relative position of the energy shells involved. For electron bombardment of high Z elements, Auger electron emission predominates and for bombardment of low Z elements, "soft" (low energy) X-rays predominate.

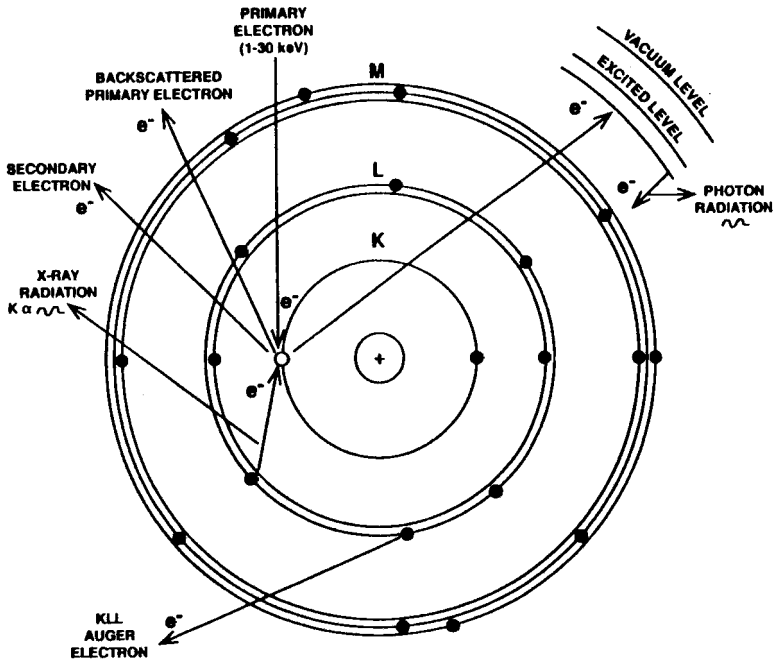


Figure 2-4. Events that can occur during electron-atom collisions.

The ejected Auger electron is identified by the shell which had the vacancy, the energy level which provided the electron to fill the vacancy and the level from which the Auger electron originated. Thus a KLL Auger electron originated from the L energy level due to an electron from the L level filling a vacancy in the K level. For example, aluminum has three principal KLL Auger electrons the primary one being at about 1400 eV. Lithium has one principal KLL Auger electron at about 30 eV. Lead has five principal MNN Auger electrons the primary one being at about 2180 eV.

The x-ray radiation that is emitted is identified by the core-level of the vacancy and the level from which the electron that fills the vacancy originates. For example, K*alpha* radiation occurs when a vacancy in the K-shell is filled by an electron from the L-shell (Cu K*alpha* energies are 8.047 and 8.027 keV) and Kß is an electron from the M-shell filling a vacancy in the K-shell (Cu Kß energies are 8.903, 8.973 and 8.970 keV). The energy of the characteristic radiation from a particular transition covers a large energy range. For example, Ti - K*alpha* = 4.058 keV and Zr - K*alpha* = 15.746 keV.

2.3.3 Chemical Bonding

The molecule is a grouping of atoms to form the smallest combination that can be associated with the chemical properties of a specific material. The molecule can range from a simple association of several atoms such as H_2 and H_2O, to molecules containing many thousands of atoms such as polymer molecules. A radical is a fragment of a molecule, such as OH^-, which would generally like to react to form a more complex molecule. The molecular structure is closely associated with the type of chemical bonding, bond orientation and bond strengths between the atoms.

Ionic bonding occurs when one atom loses an electron and the other gains an electron to give strong coulombic attraction. Covalent bonding occurs when two atoms share two electrons; for example, the carbonyl radical CO (C=O) where the electrons are shared equally. In ionic and covalent bonding there are few “free electrons” so the electrical conductivity is low. Polar covalent bonding occurs when two atoms share two electrons but the electrons are closer to one atom than the other, giving a polarization to the atom-pair. For example, the water molecule is strongly polar and likes to bond to materials by polarization. Metallic bonding is when the atoms are immersed in a “sea” of electrons which provides the bonding. Metallically bonded materials have good electrical conductivity. In some

materials there is a mixture of bond types. Van der Waals or dispersion bonding occurs between non-polar molecules when a fluctuating dipole in one molecule induces a dipole in the other molecule and the dipoles interact, giving bonding. The surface of solid polymers consists of a homologous mixture of dispersion and polar components in differing amounts for the various polymers. For example, polyethylene and polypropylene surfaces have no polar component only dispersion bonding.

2.3.4 Probing and Detected Species

In surface chemical analysis, the probing species may be electrons, ions or photons such as x-rays, optical photons or infrared photons. The detected species may be electrons, ions, or photons.

Energetic electrons are one type of probing species and they easily penetrate into the surface of a solid so electron analysis of a surface uses low energy (a few keV) electrons. The penetration is dependent not only on the energy of the electron but also the density of the material. For example, a 1.5 keV electron will penetrate about 1000 Å into a solid of density 1 g/cm^3 but it will take an electron of energy 8 keV to penetrate that far into a solid of density 20 g/cm^3. Figure 2-5 depicts the penetration of an energetic electron into a surface and the depth from which the detected species can escape (escape depth).

Energetic ions are another type of probing species and they have much less penetration than the electrons. Below about 50 keV, ions lose their energy by physical collisions ("billiard-ball" collisions) with the lattice atoms. An energetic ion will penetrate into a solid with a range of about 10Å per keV of ion energy. In an oriented lattice structure, the ion can penetrate further by being "channeled" along open (less dense) lattice planes ("channeling").

Bombardment of a surface by energetic ions can give rise to backscattering of the bombarding species from the surface and near-surface atoms, and atoms or ions (positive and negative) sputtered from the surface. The energy and number of the bombarding species that are backscattered from the surface and the energy and number of sputtered atoms depends on the relative masses of the particles in collision and the angle of collision.

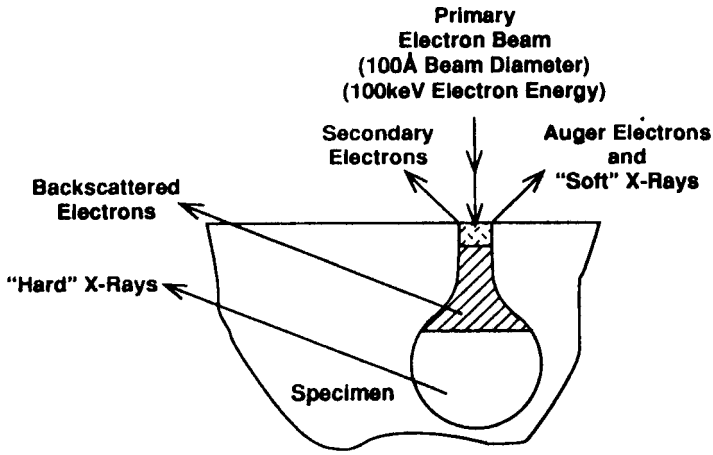
X-ray photons can be used as the probing species. Bombardment of a surface by X-rays can give rise to X-rays having a characteristic energy or electrons (photoelectrons) having a characteristic energy.

X-rays are absorbed depending on the X-ray Mass Adsorption Coefficients of the material. The adsorption is given by:

Eq. (1) $I = I_0 e^{-u/p}$

where I_0 is the intensity at the surface
u = adsorption per centimeter
[u/p = mass adsorption coefficient]
p = density of the material

u/p for beryllium at 2.50 Å wavelength radiation = 6.1; at 0.200 Å = 0.160
u/p for tungsten at 0.710 Å wavelength radiation = 104; at 0.200 Å = 3.50



Signal	Escape Depth (Å)	Effective Diameter (Å)
Photoelectrons	3	100
Auger Electrons/"Soft" X-Rays	10	100
Secondary Electrons	100	100
Backscattered Electrons	3,000-10,000	3,000-10,000
"Hard" X-Rays	5,000-30,000	5,000-30,000

Figure 2-5. Escape depths of various species formed by high-energy electrons penetrating into a solid.

High energy electron bombardment of a surface (x-ray target) provide energetic X-rays for analytical applications. Copper is a common target material since it can easily be cooled.

Copper (K *alpha*) radiation	= 1.544 Å
Tungsten (K *alpha*) radiation	= 0.214 Å

Optical photons (0.1–30 microns wavelength) are used as probing species and will penetrate solids with a great deal of variation depending on the number of conduction electrons or chemical bonds available for absorption of energy. The adsorption is given by the extinction coefficient or the opacity (or its logarithm, the optical density). About 1000 Å of a fully dense gold film will completely extinguish optical transmission as far as the eye can determine.

The wave nature of optical, x-ray and electron radiation allows the diffraction of radiation from crystal planes (both bulk—XRD, and surface—LEED, RHEED).[13]-[16] Diffraction treats each atom as a scattering center and if the scattered radiation from the points is "in phase" there is constructive interference and a strong signal. This signal position and its intensity is dependent on the separation between diffracting points and the number of points on a particular plane.

The probing species can introduce damage into the surface being analyzed by heating or atomic displacement. Ion bombardment does both, while electron bombardment damage is primarily due to heating. The extent of the damage is a function of the dose and flux of the bombarding species and the heat dissipation available. Bombardment can also cause charge build-up on insulating surfaces causing problems with some analytical techniques. In some cases this can be overcome by coating the surface with an electrically conductive layer prior to analysis.

In some analytical techniques sputter profiling is used. Sputter profiling uses sputter erosion to remove material and then the exposed surface or near-surface region is analyzed. Sputter profiling introduces some unknowns in that the sputtering process can change the surface topography, atoms may move about on the surface rather than be sputtered and heating and damage from bombardment can cause diffusion or thermal vaporization.

2.4 CHARACTERIZATION OF SURFACES AND NEAR-SURFACE REGIONS

Characterization can be defined as determining some characteristic or property of a material in a defined and reproducible way. The

characterization is often used in a comparative manner so it is relative to a previous measurement. This type of characterization should be precise not necessarily accurate. Characterization can be at all levels of sophistication and expense. Several questions should be asked before a characterization strategy is defined:

- **Is the substrate reproducible?** If not, then this aspect of the characterization should be addressed.
- Who will do the characterization? If someone else is doing the characterization, are the right questions being asked and the necessary background information been given?
- Who is going to determine what the results mean?
- How is the information going to be used?
- Has variability within a lot and from lot-to-lot been considered?
- In development work—have the experiments been properly designed to give the information needed and to establish limits on properties of interest?
- Who determines what is important and the acceptable limits?
- How quickly is the information needed? (feedback)
- Is everything being specified that needs to be specified in order to get the product/function desired?
- Is there over-specification—i.e. specifying things that are unimportant or to a greater accuracy than is needed?
- Are the functional/reliability requirements and limits on precision and accuracy of measurements reasonable?
- Is the statistical analysis correct for the application? Is the sampling method statistically correct?
- Are absolute or relative (comparative) measurements required? Precision or accuracy or both.

Substrate surfaces should be characterized early in the processing sequence. Characterization can include:

- Elemental chemical composition
- Morphology (roughness, porosity)
- Mechanical properties (strength, elasticity, deformation)

- Microstructure (phase, grain size, orientation etc.)
- Surface energy
- Acid-base nature (polymers)
- Bulk and near-surface properties important to surface behavior—ougassing, hardness, etc.

Many of the techniques used to characterize the elemental, phase, and chemical bonding nature of the material require a knowledge of the atomic and molecular nature of matter and the interaction of probing species with the atoms and molecules.

2.4.1 Elemental (Chemical) Compositional Analysis

The chemical composition of the surface is important to the nucleation and interface formation stages of film growth (Ch. 9). For example, the presence of a hydrocarbon contaminant on the surface can prevent the chemical interactions desirable for obtaining a high nucleation density during film deposition. In addition the chemical composition can have an effect on the strength of the interface and thus the adhesion.

The analysis of the chemical composition of a surface is done using surface-sensitive elemental analysis techniques.[17] There are a number of surface analysis techniques including those involving probing species of electrons (Auger Electron Spectroscopy—AES), ions (Ion Scattering Spectroscopy—ISS, and Secondary Ion Mass Spectroscopy—SIMS) and photons (X-ray Photoelectron Spectroscopy—XPS). In some cases, the nature of the chemical bonding of the surface atoms is determined by using X-ray Photoelectron Spectroscopy (XPS) or Infrared (IR) Spectroscopy (FTIR). Generally only the first few atomic layers on the surface is important to the nucleation of the depositing film material but the near-surface region may be important to interface formation. Analytical techniques for analyzing the composition of the near-surface region include Rutherford Backscattering (RBS), Nuclear Reaction Analysis (NRA), Electron probe X-ray microanalysis (EPMA) and SEM-EDAX.

The problem with many of these analytical tools is that they can only sample a small area of the substrate, whereas local problems, such as surface inclusions which generate pinholes in the deposited films, may be restricted to a small area and can be easily missed.

Auger Electron Spectroscopy (AES)

AES is a surface sensitive analytical technique that utilizes the Auger electrons that are emitted from a surface when it is bombarded (excited) by an incident high energy (1-30 keV, 0.05–5 microamps) electron beam.[18]-[22] The ejected Auger electrons have characteristic energies (few tens of eV for light element KLL electrons to 2000 eV for heavy element MNN electrons) and these energy peaks are superimposed on a continuum of electron energies in the analyzed electron energy spectrum. These peaks can be resolved by double differentiation of the electron energy spectrum. Figure 2-6 shows the "raw" electron energy spectrum and the Auger spectrum after the background spectra eliminated. Energetic electrons rapidly lose energy when moving through a solid so the characteristic energy of the Auger electrons is only preserved if the electrons escape from the first few monolayers (<10 Å) of the surface ("escape depth") so AES is a very surface sensitive analytical tool. In-depth profile analysis can be made by eroding the surface by sputtering or chemical means and analyzing the new surface.[23]

Auger electrons are not emitted by helium and hydrogen and the sensitivity increases with atomic number. The detection sensitivity ranges from about 10 at% (atomic percent) for lithium to 0.01 at% for uranium. AES can detect the presence of specific atoms but to quantify the amount requires calibration standards which are close to the composition of the sample. With calibration, composition can be established to ±10%. Where there is a mixture of several materials, some of the Auger peaks can overlap but by analyzing the whole spectrum the spectrum can be deconvoluted into individual spectra. Electron beams can be focused to small diameters so AES can be used to identify the atomic content of very small (submicron) particles as well as extended surfaces. The secondary electrons emitted by the probing electron bombardment can be used to visualize the surface in the same manner as Scanning Electron Microscopy (SEM). Thus the probing beam can be scanned over the surface to give an SEM micrograph of the surface and an Auger compositional analysis of the surface.

In PVD processing, AES is used to establish the reproducibility of the chemistry of the surface of the as-received substrate material, the effect of surface preparation on the substrate surface chemistry and the composition of the surface of the deposited film. Profiling techniques can be used to determine the in-depth composition and some information about the interfacial region.

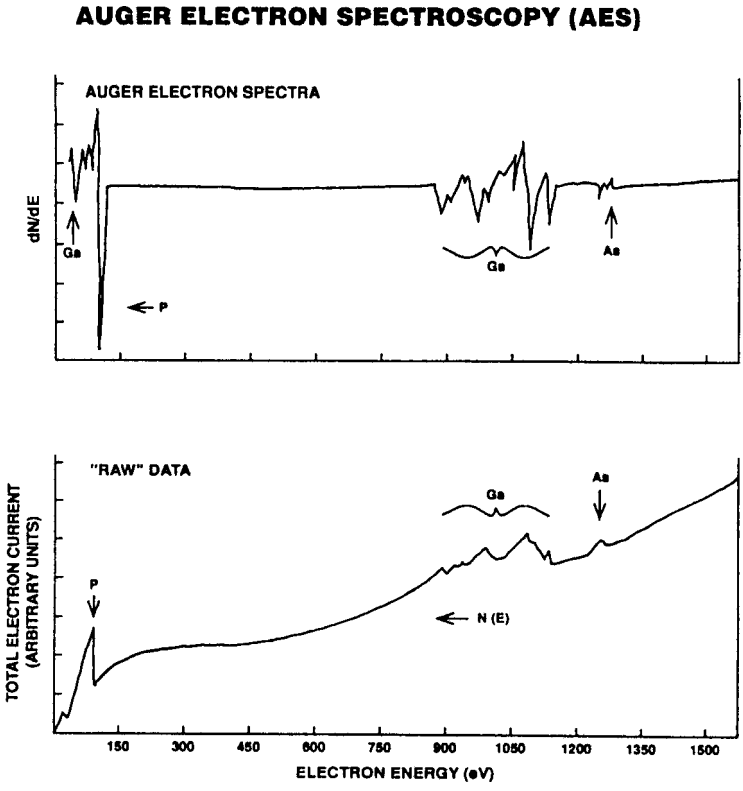


Figure 2-6. The "raw"electron spectra of a GaAs surface being bombarded with energetic electrons and the Auger electron spectra after the background has been eliminated.

Ion Scattering Spectroscopy (ISS and LEISS)

Ion Scattering Spectrometry (ISS) and low-energy ISS (LEISS) are surface sensitive techniques that take advantage of the characteristic energy loss suffered by a low energy bombarding particle on collision with a surface atom.[24] The low energy of the impinging and scattered ions differentiates it from high-energy ion scattering used in Rutherford Backscattering Spectroscopy (RBS) (Sec. 10.5.10) which penetrate into the solid. The energy loss of the reflected particle is dependent on the relative masses of the colliding particles and the angle of impact as given by Eq. 2 and Fig. 7.

From the Laws of Conservation of Energy and the Conservation of Momentum the energy, E_t, transferred by the physical collision between hard spheres is given by:

Eq. (2) $E_t/E_i = 4\ M_t M_i \cos^2\theta/(M_i + M_t)^2$

where i = incident particle
t = target particle
E = energy
M = mass
θ is the angle of incidence as measured from a line joining their centers of masses.

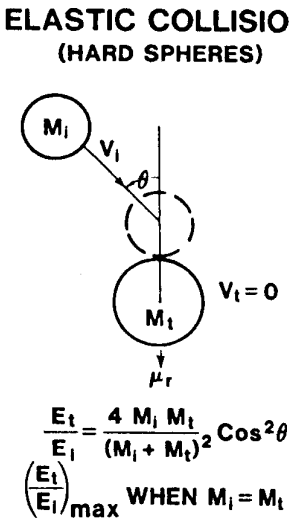


Figure 2-7. Collision of particles.

The maximum energy is transferred when $\cos\theta = 1$ (zero degrees) and $M_i = M_t$.

Most commercial ISS equipment only analyze for charged particles and particles that are neutralized on reflection are lost. The energy of the scattered ion is typically analyzed by an electrostatic sector analyzer or a cylindrical mirror analyzer. Ions for bombardment are provided by an ion source. Depth profiling can be done using sputter profiling techniques.

ISS is capable of analyzing surface species with detection limits of >0.1 at% for heavy elements and >10 at% for light elements. Mass resolution is poor for mixtures of heavy elements, and surface morphology can distort the analysis results since the scattering angle can change over the surface.

Secondary Ion Mass Spectrometry (SIMS)

Secondary Ion Mass Spectrometry (SIMS) is a surface analytical technique that utilizes the sputtered positive and negative ions that are ejected from a grounded surface by ion bombardment. The ejected ions are mass analyzed in a mass spectrometer.[25]-[28] The ions may be in an atomic or molecular form and may be multiply charged. For instance, the sputtering of aluminum with argon, yields Al^+, Al^{2+}, Al^{3+} Al_2^+ Al_3^+ and Al_4^+. When molecules are present, the sputtering produces a complex distribution of species (cracking pattern). The technique can analyze trace elements in the ppm (parts per million) and ppb (parts per billion) range.

The degree of ionization of the ejected particles is very sensitive to surrounding atoms ("matrix effect") and the presence of more electronegative materials such as oxygen. For example, the aluminum ion yield per incident ion from an oxide-free surface of aluminum is 0.007, but if the surface is covered with oxygen the yield is 0.7. To quantify the analysis requires the development of standards. The problem of low ion yield and matrix effect can be avoided by post-vaporization ionization of the sputtered species. This technique is called Secondary Neutral Mass Spectrometry (SNMS). Since the detected species are sputtered from the surface, the technique is very surface-sensitive. The matrix effect and the ability of atoms to move about on the surface makes sputter profiling through an interface with SIMS very questionable. Since ion beams cannot be focused as finely as electron beams the lateral resolution of SIMS is not as good as that of AES.

2.4.2 Phase Composition and Microstructure

In some applications the crystallographic phase composition, grain size, and lattice defect structure of a surface can be important. Phase composition is generally determined by diffraction methods.

X-ray Diffraction

When a crystalline film is irradiated with short wavelength X-rays the crystal planes can satisfy the Bragg diffraction conditions giving a diffraction pattern. This diffraction pattern can be used to determine the

crystal plane spacing (and thus the crystal phase), preferential orientation of the crystals in the structure, lattice distortion, and crystallite size.[29]

Electron Diffraction (RHEED, TEM)

The diffraction of electrons can be used to determine the lattice structure.[30] The diffraction can be of a bulk (3-dimensional) material or can be from a surface. Reflection High Energy Electron Diffraction (RHEED) is used in epitaxial film growth to monitor film structure during deposition. Electron diffraction can be used in conjunction with Transmission Electron Microscopy (TEM) to identify crystallographic phases seen with the TEM. This application is called electron microdiffraction or Selected Area Diffraction or TEM-SAD.[31]

2.4.3 Molecular Composition and Chemical Bonding

Infrared (IR) Spectroscopy

A polymer is a large molecule formed by bonding together numerous small molecular units, called monomers. The most common polymeric materials are the organic polymers which are based on carbon-hydrogen (hydrocarbon) monomers which may or may not contain other atoms such as nitrogen, oxygen, metals, etc. In building a polymer, many bonds are formed which have various strengths and separations (bond lengths) between atoms.

Infrared spectroscopy uses the adsorption of infrared radiation* by the molecular bonds to identify the bond types which can absorb energy by oscillating, vibrating and rotating.[32] The adsorption spectrum is generated by having an continuum spectrum of infrared radiation pass through the sample and comparing the emerging spectra to that of a reference beam that has not passed through the sample. In dispersive infrared spectrometry a monochromator separates light from a broad-band source into individual narrow bands. Each narrow band is then chosen by a mechanical slit arrangement and is passed through the sample. In Fourier Transform infrared spectrometry (FT-IR) the need for a mechanical slit is

*Infrared radiation is electromagnetic radiation having a wavelength greater than 0.75 microns.

eliminated by frequency modulating one beam and using interferometry to choose the infrared band. This technique gives higher frequency resolution and a faster analysis time than the dispersive method.

By having a spectrum of adsorption vs infrared frequency, the type of material can often be identified. If the material cannot be identified directly, then the types of individual bonds can be identified giving a good indication of the type of polymer material. It can also be used to characterize polymer substrate materials as to their primary composition and such polymer additives as plasticizers, anti-slip agents, etc. The IR spectrum of many materials are cataloged and a computer search is often used to identify the material.

Sample collection is an important aspect of IR analysis. Bulk materials can be analyzed but if they are thick, the sensitivity of the technique suffers. Often the sample is prepared as a thin film on the surface of an IR transparent material (window) such as potassium bromide (KBr). The film to be analyzed can be formed by condensation of a vapor on the window, dissolving the sample in a solvent, then drying to a film or by solvent extraction from a bulk material followed by evaporation of the solution on an IR window. Figure 2-8 shows an IR spectra of a phythale plasticizer extracted from a vinyl material by extraction using acetone. This type of plasticizer is often used in polymers to make them easier to mold and is a source of contamination by outgassing, outdiffusion and extraction of the low molecular weight materials by solvents such as alcohol (Sec. 13.3.1).

Reflection techniques can often be used to analyze surface layers without using solvent extraction. A reflection technique is shown in Fig. 8 where the sample is sandwiched between plates of a material having a high index of refraction in the infrared so as to have a high reflectivity from the surface.

In PVD technology, IR spectroscopy is used in a comparative manner to insure that the substrate material is consistent. Quite often it is found that a specific polymer material from one supplier will differ from that of another in the amount of low-molecular weight constituents present. This can affect the outgassing and outdiffusion of material from the bulk during processing and the postdeposition behavior of the film surface.* The

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*The producer metallized web materials for labeling applications but sometimes the users complained that they couldn't print on the metallized surface. The problem was the low molecular weight species in the web was diffusing through the metallization and forming a low-energy polymer surface on the metallization. The manufacturer needed to have a better web material.

low-molecular weight materials can originate from an additive material or from differing curing of the monomer materials. A procedure to characterize a polymeric material might consist of:

- A "swipe" or solvent clean of the surface of the as-received material to determine if there is a surface layer of low molecular weight species.
- Solvent extraction from the bulk material using a given sample area, solvent, solvent concentration, temperature and time.
- Vacuum heating for a specific time at a specific temperature followed by solvent extraction to ascertain outdiffusion and surface contamination by low molecular weight species.
- Vacuum heating for a specific time and temperature with a cool IR window in front of the surface to collect volatile species resulting from outgassing of the bulk material.

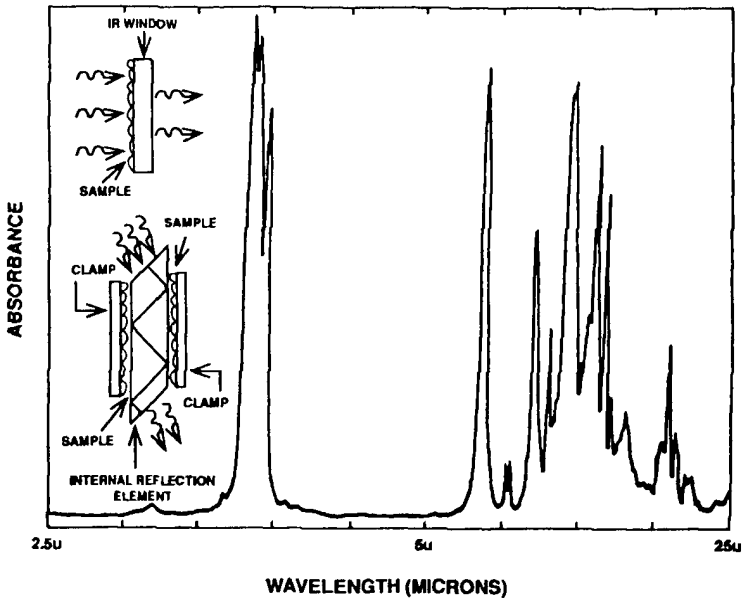


Figure 2-8. Infrared (IR) spectrum of a phthalate plasticizer extracted from a vinyl material.

These spectra would then form a baseline with which to compare subsequent as-received material. These same procedures could be used to characterize the polymer surface after surface preparation processing such as an oxygen plasma treatment or the application of a basecoat.

In PVD processing, IR spectroscopy can be used to identify such common contaminants as hydrocarbon, silicone and fluorinated pump oils, hand creams, adsorbed hydrocarbons, etc. System and process-related contamination can be studied by IR spectroscopy techniques. For example, an IR window can be placed in front of the roughing port of a deposition system during cycling and IR analysis will show if there is any backstreaming of the roughing pump oils. The same can be done in front of the high vacuum port to detect backstreaming from the high vacuum pumping system. During processing, a window can be placed out-of-line-of-sight of the vaporization source to detect volatile/condensable species that may not be detectable using a residual gas analyzer (RGA). IR spectroscopy can also be used to identify bonding in non-polymeric materials. For example, the transmission spectra of float glass will show the absorption in the glass due to iron oxide.

X-ray Photoelectron Spectroscopy (XPS) or Electron Spectroscopy for Chemical Analysis (ESCA)

X-ray Photoelectron Spectroscopy (XPS) or, as it is sometimes called, Electron Spectroscopy for Chemical Analysis (ESCA), is a surface-sensitive analytical technique that analyzes the energy of the photoelectrons (50–2000 eV) that are emitted when a surface is bombarded with X-rays in a vacuum.[33]-[36] The energy of these electrons is characteristic of the atom being bombarded and thus allows identification of elements in a similar manner to that used in Auger Electron Spectroscopy (AES).

Photoelectron emission occurs by a direct process where the X-ray is absorbed by an atomic electron and the emitted electron has a kinetic energy equal to that of the energy of the incident X-ray minus the binding energy of the election. In contrast to the characteristic electron energies found in Auger Electron Spectroscopy (AES), the XPS photoelectrons depend on the energy of the X-rays used to create the photoelectrons and both monochromatic and non-monochromatic X-ray beams are used for analysis. Typically the K*alpha* X-ray radiation from magnesium (1253.6 eV) or aluminum (1486.6 eV) is used for analysis. The energy of the ejected electron is usually determined using a velocity analyzer such as a

cylindrical mirror analyzer. The Auger electrons show up in the emitted electron spectrum but can be differentiated from the photoelectrons in that they have a characteristic energy that does not depend on the energy of the incident radiation.

The photoelectrons can come from all electronic levels but the electrons from the outer-most electronic states have energies that are sensitive to the chemical bonding between atoms. Information on the chemical bonding can often be obtained from the photoelectron emission spectra by noting the "chemical shifts" of the XPS electron energy positions. For example, AES can detect carbon on a surface but it is difficult to determine the chemical state of the carbon. XPS detects the carbon and from the chemical shifts can tell if it is free carbon or carbon in the form of a metal carbide.

Figure 2-9 shows the X-ray photoelectron spectrscopy (XPS) spectrum with the energy position of silicon as pure silicon, as Si_3N_4 and as oxidized Si_3N_4. The spectra show the chemical shift between the different cases. The XPS analytical technique avoids the electron damage and heating that is sometimes encountered in AES. XPS is the technique used to determine the chemical state of compounds in the surface—for example, the ratio of iron oxide to chromium oxide on an electropolished stainless steel surface or the amount of unreacted titanium in a titanium nitride thin film. The spatial resolution of the XPS technique is not as good as with AES since X-rays cannot be focused as easily as electrons.

XPS is one of the primary techniques for analyzing the elemental, chemical, and electronic structure of organic materials.[37] For example, it can determine the chemical environment of each of the carbon atoms in a hydrocarbon material.

2.4.4 Surface Morphology

The morphology of a surface is the nature and degree of surface roughness.[38]-[43] This may be of the surface in general or of surface features. This substrate surface morphology, on the micron and submicron scale, is important to the morphology of the deposited film, the surface coverage, and the film properties. The surface roughness (surface finish) can be specified as to the $\mathbf{R_a}$ finish, which is the arithmetic mean of the departure of the roughness profile from a mean line (microinches, microns) as shown in Fig. 2-10. The $\mathbf{R_{max}}$ is the distance between two lines parallel to the mean line which contact the extreme upper and lower profiles.

Measuring the surface roughness this way does not tell much about the morphology of the roughness which is important to whether a deposited film can "fill-in" the valleys between the peaks.

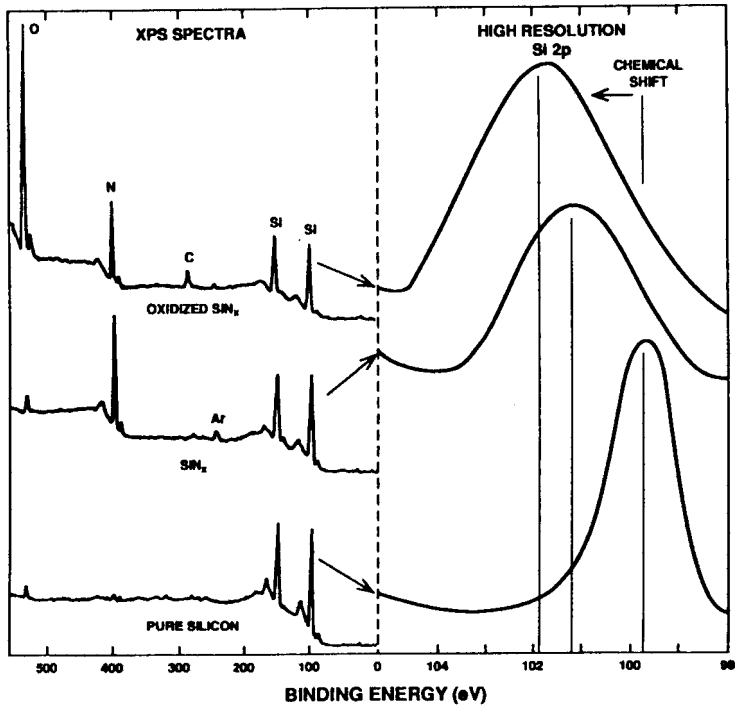


Figure 2-9. X-ray Photolectron Spectroscopy (XPS) spectra of Si_3N_4 film with and without oxygen contamination.

Profilometers are instruments for measuring (or visualizing) the surface morphology. There are two categories of surface profilometers. One is the contacting type which uses a stylus in contact with the surface that moves over the surface and the other is the non-contacting type which does not contact the surface. The contacting types can deform the surface of soft materials Some of the profilometer equipment can be used in several modes. For example, one instrument might be used in a contacting or non-contacting Atomic Force Microscope (AFM) mode, a Scanning Tunneling Microscope (STM) mode, as a magnetic force (magnetic force measuring) microscope, or as a lateral force (friction measuring) instrument.

In more advanced profilometers, using a mechanical stylus or probe, the movement (position) of the probe can be monitored using a reflected laser beam in an optical-lever configuration or by a piezoelectric transducer or by displacement interferometry.

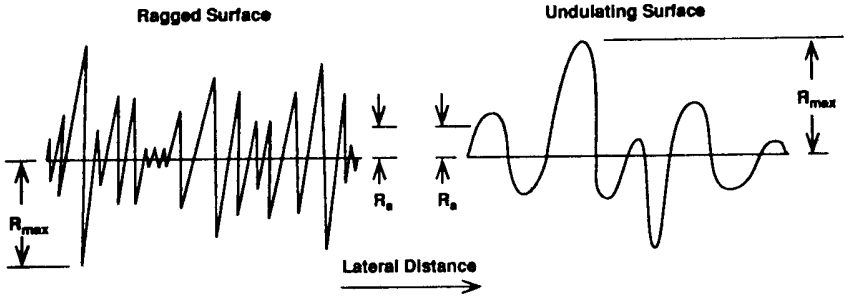


Figure 2-10. Surface roughness.

Contacting Surface Profilometry

Stylus profilometers use a lightly-loaded stylus (as low as 0.05 mg) to move over the surface and the vertical motion of the stylus is measured.[44][45] The best stylus profilometers can give a horizontal resolution of about 100 Å and a vertical resolution as fine as 0.5 Å, although 10–20 Å is more common. In the scanning mode, the profilometer can give a 3-D image of the surface from several hundreds of microns square to several millimeters square. The ability of the stylus profilometer to measure the depth of a surface feature depends on the shape of the profilometer tip and tip shank. Stylus profilometers have the advantage that they offer long-scan profiling, ability to accommodate large-sized surfaces and pattern recognition. The pattern recognition capability allows the automatic scanning mode to look for certain characteristics, then drive automatically to those sites—allowing a "hands-off" operational mode.

Scanning Tunneling Microscopy (STM) and Atomic Force Microscopy (AFM)

The Scanning Tunneling Microscope (STM) and its predecessor the "topographfinder,"[46] is based on the principle that electrons can tunnel through the potential barrier from a fine tip to an electrically conductive surface if a probe tip is close enough (several angstroms) to the conductive surface.[47]-[49] The system is typically operated in a constant-tunneling-current mode as a piezoelectric scanning stage moves the sample. The vertical movement of the probe is monitored to within 0.1 Å. Under favorable conditions, surface morphology changes can be detected with atomic resolution. The findings are often very sensitive to surface contamination. At present, the STM can only be used on conductive surfaces but techniques are being developed, using rf potentials, that will allow its use on insulating surfaces.

The Atomic Force Microscope (AFM), which is sometimes called the Scanning Force Microscope (SFM), is based on the forces experienced by a probe as it approaches a surface to within a few angstroms.[50]-[55] A typical probe has a 500 Å radius and is mounted on a cantilever which has a spring constant less than that of the atom-atom bonding. This cantilever spring is deflected by the attractive van der Waals (and other) forces and repulsed as it comes into contact with the surface ("loading"). The deflection of the spring is measured to within 0.1 Å. By holding the deflection constant and monitoring its position, the surface morphology can be plotted. Because there is no current flow, the AFM can be used on electrically conductive or non-conductive surfaces and in air, vacuum, or fluid environment. The AFM can be operated in three modes: contact, non-contact and "tapping." The contact mode takes advantage of van der Waal's attractive forces as surfaces approach each other and provides the highest resolution. In the non-contacting mode, a vibrating probe scans the surface at a constant distance and the amplitude of the vibration is changed by the surface morphology. In the tapping mode, the vibrating probe touches the surface at the end of each vibration exerting less pressure on the surface than in the contacting mode. This technique allows the determination of surface morphology to a resolution of better than 10 nm with a very gentle contacting pressure (Phase Imaging). Special probe tip geometries allow measuring very severe surface geometries such as the sidewalls of features etched into surfaces.[56][57]

Interferometry

The Scanning White Light Interferometer generates a pattern of constructive (light) and destructive (dark) interference fringes resulting from the optical path difference from a reference surface and the sample surface thus showing the topography of the surface.[58][59] In an advanced scanning system a precision translation stage and a CCD camera together generate a three-dimensional interferogram of the surface that is stored in a computer memory. The 3D interferogram is then transformed into a 3D image by frequency domain analysis. One commercial scanning interferometer can scan a surface at 1.0 microns (μm)/s to 4 μm/s with a lateral resolution of 0.5 μm to 4.87 μm and a field of view of 6.4 mm to 53 μm depending on the magnification. It can measure the height of surface features up to 100 microns with a 1 Å resolution and 1.5% accuracy, independent of magnification. Typical imaging time for a 40 μm scan is less than 30 seconds. Interferometry is also used to measure the beam deflection when making film stress measurements (Sec. 10.5.1). The combination of the Atomic Force Microscope and interferometry has produced the Scanning Interferometric Aperatureless Microscope (SIAM) that has a resolution of about 8 Å.[60]

Scanning Near-Field Optical Microscopy (SNOM) and Photon Tunneling Microscopy (PTM)

Surfaces can be viewed by optical microscopy but the resolution of a standard optical microscope is diffraction limited to a lateral resolution of about 5000Å with a poor depth of field at high magnifications. The strict optical analog of electron tunneling in the STM, is the tunneling of photons in the Scanning Near-field Optical Microscope (SNOM) which uses an optical probe very near the surface.[61][62] As the probe is brought further away from the surface the resolution decreases, however the vertical resolution is preserved and it is in this regime that the Photon Tunneling Microscope (PTM) operates.[63] The sample surface must be a dielectric for the PTM to function. The vertical resolution of the PTM is about the same as the SEM, however the lateral resolution is less.

Scatterometry

Scatterometry measures the angle-resolved scattering of a small spot (about 30 μm) of laser-light from a surface.[64]-[66] The distribution of the scattered energy is determined by the surface roughness. The scattering is sensitive to dimensions much less than the wavelength of the light used. Scatterometry can be used to characterize submicron sized surface features possibly as small as 1/20 of the wavelength of the incident light. From the spatial distribution, the root mean square (rms) roughness can be calculated. The technique is particularly useful for making comparative measurements of substrate surface roughness.

Scanning Electron Microscope (SEM)

A surface can be viewed in an optical-like form using the Scanning Electron Microscope (SEM). Instead of light, the SEM uses secondary electrons emitted from the surface to form the image.[67][68] The intensity and angle of emission of the electrons depend both on the surface topography and the material.[69] The angle of emission depends on the surface morphology so the spatially-collected electrons allow an image of the surface to be collected and visually presented. The magnification of the SEM can be varied from several hundred diameters to 250,000 magnification. However the image is generally inferior to that of the optical microscope at less than 300x magnification. The technique has a high lateral and vertical resolution. Figure 2-2 shows the surface of a sintered 96% alumina ceramic commonly used as a substrate for microelectronic fabrication. Stereo imaging is possible in the SEM by changing the angle of viewing of the sample. This can be done by rotating the sample along an axis normal to the electron beam.

Replication TEM

Surfaces can be visualized by replicating the surface with a removable film, shadowing the replica and then using the Transmission Electron Microscope (TEM) described in Sec. 10.5.12.

Adsorption—Gases and Liquids

Gas and fluid absorption can be used to measure the absorption on the surface which is proportional to the surface area.[70] Adsorption of radioactive gases such as Kr^{85} allows the autoradiography of the surface.[71] This type of analysis allows the relative characterization of the whole surface. Figure 2-11 shows a Kr^{85} autoradiograph of a 96% sintered alumina surface shown in Fig. 2-2 using the SEM. The difference is that the autoradiograph is of a standard 4 x 4 inch substrate while the SEM covers an area about 0.001 x 0.001 inches.

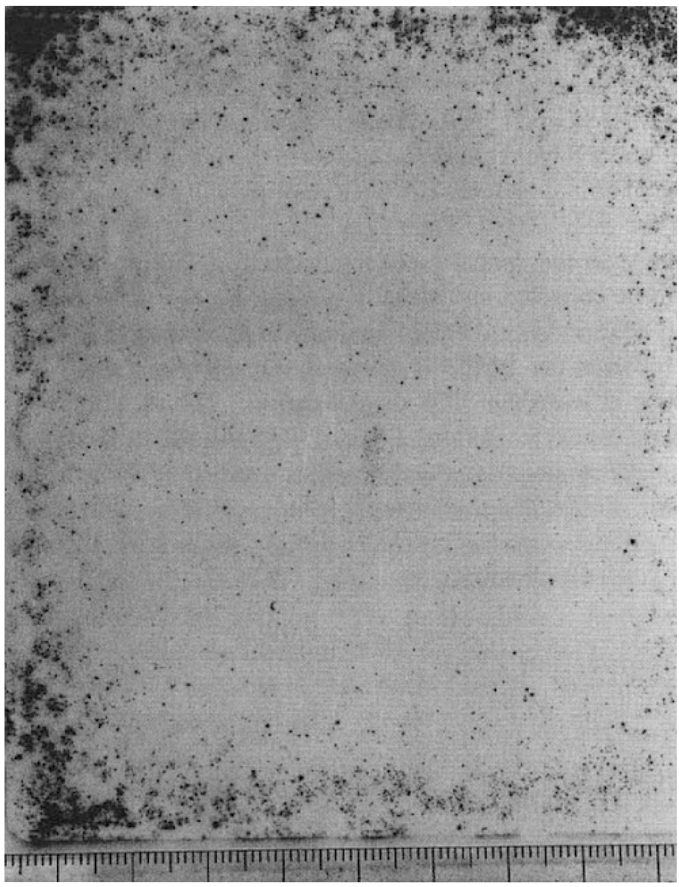


Figure 2-11. Kr^{85} autoradiograph of a sintered alumina surface.

Using xenon gas absorption, increases in the absorption area over the geometrical area of factors of 2 to 3 have been measured.[72] Instead of radioactive gases, fluorescent dyes can be used to directly visualize the substrate surface for local variations in porosity. Surface acoustic wave (SAW) adsorption can also be used to measure surface roughness and porosity.[73]

2.4.5 Mechanical and Thermal Properties of Surfaces

The mechanical properties of the substrate surface can be an important factor in the functionality of the film-substrate structure. For example, for wear-resistant films, the deformation of the substrate under loading may be the cause of failure. If the substrate surface fractures easily, then the apparent adhesion between the film and the substrate will be low.

Hardness is usually defined as the resistance of a surface to permanent plastic deformation.[74][75] The Vickers (HV) or Knoop (HK) hardness measurements are made by pressing a diamond indenter, of a specified shape, into a surface with a known force. The hardness is then calculated by using an equation of the form:

Eq. (2) Hardness (HV or HK) = constant (HV_{const} or HK_{const}) x p/d^2 (Kg/mm^2)

where p is the indentation force and d is a measured diagonal of the indenter imprint in the surface. To be valid, the indentation depth should be less than 1/10th of the thickness of the material being measured. By observing the fracturing around the indentation, some indication of the fracture strength (fracture toughness) of the surface can be made.

When the material to be tested is very thin, the indentation should be shallow and the applied load small. This is called microindentation hardness[76]-[78] or "nanoindentation"[79][80] and the indentation load can be as low as 0.05 milligrams. One commercial instrument is capable of performing indentation tests with load of 2.5 millinewtons and depth resolutions of 0.4 nanometers. It detects penetration movement by changes in capacitance between stationary and moving plates. When the load is distributed over an appreciable area (Hertzian force), elastic effects and surface layers, such as oxides, can have an important effect on the measured hardness. A technique of measuring the microindentation deformation while the load is applied ("depth-sensing"), is used to overcome these elastic effects.

Hardness measurements generally do not give much of an indication of the fracture strength of the surface. Scratch tests and stud-pull tests (Sec. 11.5.2) can provide a better indication of the fracture strength of the surface. Scratching is typically performed using a hard stylus drawn over the surface with an increasing load. The surface is then observed microscopically for deformation and fracture along the scratch path. The acoustic emission from the surface during scratching can also give an indication of the amount of brittle fracturing that is taking place during scratching. The stud-pull test is performed by bonding a stud to the surface with a thermosetting epoxy then pulling the stud to failure. If the failure is in the surface material, the failed-surfaces are observed for fracture and "pull-outs." A mechanical bend test can also be used as a comparative fracture strength test.

The thermal properties of a surface can be determined with a lateral resolution of 2000 Å using Scanning Thermal Microscopy (SThM).[81] The scanning tip is in the form of a thermocouple which is heated by a laser. The thermal loss to the surface of a bulk or thin film is then measured.

2.4.6 Surface Energy

Surface energy (surface tension) is an important indicator of surface contamination and the composition of a polymer surface. The surface energy results from non-symmetric bonding of the surface atoms/molecules in contact with a vapor, and is measured as energy per unit area.[82] Surface energy and surface tension differ slightly thermodynamically but the terms and values quoted are often used interchangeably. Surfaces with a high surface energy will try to lower their energy by adsorbing low energy materials such as hydrocarbons.

The surface energy and interfacial energy are measured by the "contact angle" of a fluid droplet on the solid. The contact angle is measured from the tangent to the droplet surface at the point of contact, through the droplet to the solid surface.[83]-[85] Figure 2-12 shows the contact angle of a water drop on a surface with a high surface enegy and on a surface with a low surface energy. The surface tension of a liquid can also be measured by the Wilhelmy pin test where the downward pull on a clean metal pin being withdrawn from the fluid is measured by a microbalance with an accuracy of about 1 mg. It can also be measured by the fluid rise in a capillary tube.

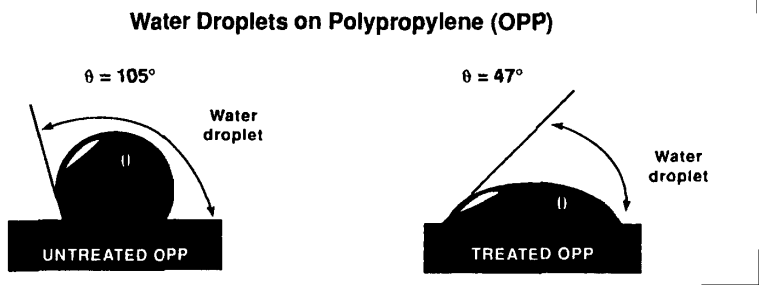


Figure 2-12. Contact angle of a water drop on a surface with a high surface energy (left) and on a surface with a low surface energy (right).

To measure the contact angle, a fluid droplet is applied to the surface using a microsyringe to give a constant volume of fluid. De-ionized water is a commonly used contacting fluid. The contact angle is then measured with a "contact angle goniometer". There are three types of goniometers. The projection-design, projects an image of the drop; the operator establishes the tangent by rotating a fiducial filar in a long-focus microscope. The microscope-based design uses a low-power microscope with an internal protractor scale to look at the image of the drop. The computerized-automated system uses a video camera to observe the image of the drop, digitize the image and a computer program establishes the tangent and calculates the contact angle. Clean metal and oxide surfaces have a high surface free energy as shown in Table 2-1.

A rough surface will affect the contact angle and particularly the values of the "advancing" and "receding" contact angles as well as the hysteresis normally found in sequential contact angle measurements. In the formation of fluid droplets, such as in spraying or in blow-drying, the size of the droplets that are formed is a function of the surface energy. The higher the surface energy the bigger the droplets that can be formed. The surface energy of fluids allows particulates, which are heavier than the fluid, to "float" on the surface of the fluid. These particles can then be "painted-on" the substrate surface as it is being withdrawn from the liquid.

Many polymers have a low surface energy and processes such as ink printing do not work well because the ink does not wet the polymer surface. *ASTM D2578-84* (dyne solution test method) is commonly used to measure the wettability of a surface. Various techniques such as corona or flame treatment in air or oxygen or nitrogen plasma treatment in vacuum

are used to increase the surface energy of polymer surfaces. For example, on properly corona-treated biaxially oriented polypropylene, the surface energy will be about 46 mJ/m^2 (contact angle = 70 degrees—de-ionize water) compared to about 33 mJ/m^2 (contact angle = 106 degrees) for the untreated surface, as shown in Fig. 2-12. For a given polymer, it is not uncommon to find variations in the surface energy of 5–10 mJ/m^2 over the surface so it is to be expected that there will be a spread in measured surface energy values after treatment and a statistically-meaningful number of measurements should be made.

Table 2-1. Surface Free Energy of Various Materials

Material	Temperature (°C)	Surface free energy (ergs/cm^2)
Cu	1000	850
Pb	300	450
Glass	25	1200
Al_2O_3	1000	900
MgO	25	1100
Polyethylene	25	30
Teflon™	25	20

2.4.7 Acidic and Basic Properties of Surfaces

An acid (Lewis acid) is an electron acceptor while a base (Lewis base) is an electron donor. The degree of acidity or basity is dependent on the materials in contact. An acidic surface will be wetted by a basic fluid while a basic surface will be wetted by an acidic fluid. A basic fluid will not wet or adhere to an acidic surface and vice versa. An amphoteric material is one that can act as either an acid or a base in a chemical reaction depending on the nature of the other material.

The reactivity of the surface to a depositing atom will vary with the tendency of the adatom to accept or donate an electron to the chemical bond.[86] Increasing the surface energy of the polymer by oxidation, forms carbonyl groups (C=O) on the surface, making the surface more acidic and thus more reactive with metal atoms which tend to oxidize such as titanium, chromium and zirconium. Plasma treatment in nitrogen or ammonia will

make the polymer surfaces more basic and not be conducive to reaction with depositing metallic atoms except for a material like aluminum which is amphoteric. Gold, which does not either accept or donate electrons has poor adhesion to both acidic and basic surfaces.

The electronic nature of a surface can be changed by changing the chemical composition. For example, the surface of a soda-lime glass is generally basic but an acid treatment will leach the sodium from the surface making a more acidic surface.

2.5 BULK PROPERTIES

Some of the bulk properties of the substrate can have an important effect on the growth and properties of the deposited film. Outgassing is the diffusion of a mobile species through the bulk of the material to the surface where it vaporizes. Gases, water vapor and solvent vapors are species that are commonly found to outgas from polymers while hydrogen outgasses from metals. Zinc that volatilizes from heated brass is another example of an outgassing species. Outdiffusion is when the mobile species that reaches the surface does not volatilize but remains on the surface as a contaminant. Plasticizers from molded polymers is an example of a material that outdiffuses from the bulk of the material. Often there is both outgassing and outdiffusion at the same time. The outgassing and outdiffusion properties of a material often depend on the fabrication and history of the material.

2.5.1 Outgassing

The outgassing from a material can be measured by vacuum baking the material and monitoring the weight-loss as a function of time using Thermal Gravametric Analysis (TGA), on the material. The volatilized species can be monitored using a mass spectrometer or can be collected on an infrared window material and measured by IR techniques. The material is said to be outgassed when the weight becomes constant or the monitored mass peak decreases below a specified value. In vacuum baking, it is important that the temperature be such that the substrate material itself is not degraded by the baking operation. The outgassing properties of the bulk material are often a major substrate variable when

using polymers. The time to outgas a material is often measured in hours and can vary with the thickness and history of the material (Sec. 12.7.2).

2.5.2 Outdiffusion

Outdiffusion is more difficult to measure than is outgassing since there is no weight change or volatilized species. The presence of the material that has outdiffused can be monitored by surface analytical techniques or by the behavior of the surface. For example, the outdiffusion of a low-molecular weight polymer to a surface can be detected by changes in the surface energy (wetting angle). In some cases this surface material can be removed by repeated conventional cleaning techniques. In some cases the out-diffusing materials must be "sealed-in" by the application of a basecoat such as an epoxy basecoat on polymers or electrodeposited nickel or nickel-chromium basecoat on brass (Sec. 2.6.4).

2.6 MODIFICATION OF SUBSTRATE SURFACES

2.6.1 Surface Morphology

The surface morphology of the substrate surface is important in determining the properties of the deposited film (Ch. 9).

Smoothing the Surface

Smooth surfaces will typically yield more dense PVD coatings than rough surfaces due to the lack of "macro-columnar morphology" resulting from geometrical shadowing of features on the substrate surface. Very smooth metal surfaces can be prepared by diamond-point machining. Mechanical polishing is commonly used to smooth surfaces.[87] Table 12-1 gives some sizes (grits) of various materials used for abrasion and polishing. Table 2-2 gives the surface finish that can be expected from polishing with various size grits. In the case of brittle materials, the polishing process can introduce surface flaws such as cracks which weaken the surface and the interface when a film is deposited. The degree of surface flaw generation is dependent on the technique used and the polishing environment. These

flaws should be blunted by wet chemical etching before the film is deposited. It has been shown that a non-hydrogen-containing polishing environment gives less fracturing than does a hydrogen-containing environment.[88] Mechanical polishing may disrupt the material in the surface region possibly producing an amorphous layer. This region can be reconstructed by heating.[89] Buffing or burnishing can be used to smooth the surfaces of soft materials such as aluminum and copper.

Table 2-2. Typical Grit Size vs Surface Finish on Polished Steel

Grit Number	Microinch Finish
500	4-16
320	10-32
240	15-63
180	85 R_{max}
120	125 R_{max}
60	250 R_{max}

Chemical polishing smooths surfaces by preferentially removing high points on the surface.[90] Often chemical polishing involves using chemicals that present waste-disposal problems. An exception is the use of hydrogen peroxide as the chemical polishing agent. Chemical and mechanical polishing can be combined to give chemical-mechanical polishing (CMP).[91][92][92a] This combination technique can often give the smoothest surfaces and is used to globally planarize surfaces in semiconductor device processing. Smooth surfaces on some metals can be formed by electropolishing. Stainless steel for example, is routinely electropolished for vacuum applications.

In some types of edge-forming processes, such as shearing and grinding, a thin metal protrusion (burr) is left on the edge. Removal of this burr ("deburring") can be done by abrasion, laser vaporization or "flash deburring," which uses a thermal pulse from an exploding gas-oxygen mixture to heat and vaporize the thin metal protrusions.

A basecoat is a layer on the surface that changes the properties of the surface. Flowed basecoats of polymers on rough surfaces are used to

provide a smooth surface for deposition. Basecoat materials of acrylics, polyurethanes, epoxies, silicones, and siloxaines are available and are very similar to the coating materials that are used for conformal coatings. In solvent-based formulations, the nature and amount of the volatile solvent evolved is of concern in order to comply with environmental concerns. Solvents can vary from water to various chlorinated solvents. "Solids content" is the portion of the formulation that will cure into a film. The balance is called the "solvent content." The solids content can vary from 10 to 50 percent depending on the material and application technique.

Coating materials can be applied by flowing techniques such as flow (curtain) coating, dip coating, spray coating, spin coating, or brush coating. The coating technique often determines the solids content of the coating material that can be used. For example in flow coating, the solids content may be 20% while for dip coating with the same material the solids content may be 35%. Flow coatings are typically air-dried (to evaporate solvent) then perhaps further cured by thermal or ultraviolet (UV) radiation. UV curing is desirable because the solvent content of the coating material is generally lower than that for thermally cured materials. The texture of the coated surface can be varied by the addition of "incompatible" additives that change the flow properties of the melt, which is useful in the decorative coating industry. In some cases the fixture used for holding the substrates while applying the basecoat is the same fixture as is used in the deposition process. In this case cleaning the fixture will entail removing a polymer film as well as removing the deposited PVD film.

An important consideration in polymer coatings is their shrinkage on curing. For example, some UV-curing systems have a shrinkage of 10-18% on curing. If the shrinkage is high the coating thickness must be limited or the coating will crack. UV-curing epoxy/acrylate resins have been developed that overcome these problems and allow curing of thick coatings (1 mil or greater) in a few seconds.

Acrylics are excellent for production coating because they are easy to apply and can be water-based as well as chlorofluorocarbon (CFC) solvent-based. The evaporation-cured acrylic coatings can be easily removed by many chlorinated solvents making rework simple. Polyurethane coatings are available in either single or two-component formulations as well as UV curing formulations. Moisture can play an important role in the curing of some polyurethane formulations. Epoxy coatings are very stable and can be obtained as two-component formulations or as UV curing single-part formulations. Silicone coatings are thermally cured and are

especially useful for abrasion-resistant and chemical-resistant coatings and for high temperature applications (to 200°C).

Powder coatings are dry powders that are typically applied to a surface by electrostatic spraying.[93] The powders are generally epoxy-based or polyester-based and the powders are flowed and cured at about 200°C in heat ovens.[93] Acrylic-based powder coatings are not very stable and are not widely used. Powder size and size distribution are important in powder coating. Smaller size powders are considered to be those less than 25 microns in diameter. If too much material is applied the surface has an "orange-peel" appearance.

Polymers can be evaporated, deposited and cured in a vacuum system to provide a basecoat. For example, acrylate coatings can be deposited and cured with an electron beam.[94] The deposited liquid flows over the surface and covers surface flaws reducing pinhole formation. This technique can be used in vacuum web coating and has been found to improve the barrier properties of transparent barrier coatings.

Roughening Surfaces

Roughening the substrate surface can be used to improve the adhesion of the film to the surface.[95] To obtain the maximum film adhesion the deposited film must "fill-in" the surface roughness.

Surfaces can be roughened by mechanically abrading the surfaces using an abrasive surface such as emery paper or an abrasive slurry. The degree of roughness will depend on the particle size used and the method of application. This rather mild abrasion will not introduce the high level of surface stresses that are created by grit blasting.

Grit blasting uses grit of varying sizes to impact and deform the surface. The grit is either sucked (siphon gun) or carried (pressure gun) into the abrasive gun where it is accelerated to a high velocity by entrainment in a gas stream. The size and shape of the grit are important to the rate of material removal and the surface finish obtained. Sharp angular grit, such as fractured cast iron grit, is most effective in roughening and removing material. Cast iron grit is often used for surface roughening. Size specifications for cast iron grit are shown in Table 2-3 (*SAE J444*). Figure 2-13 shows a copper surface roughened by grit blasting with cast iron grit.

Care must be taken when grit blasting or abrading a surface, that chards of glass or particles of grit do not become embedded in the surface. These embedded particles will cause "pinhole flaking" in the deposited

film. Water-soluble grit, such as magnesium carbonate, may be used to roughen some surfaces and any embedded particles can be removed in subsequent cleaning. High pressure (50,000 psi) water jets can be used to roughen soft materials such as aluminum without leaving embedded materials. The surface to be roughened should be cleaned before roughening to prevent contamination from being embedded and covered-over by the deformed material.



Figure 2-13. Copper surface roughened by grit blasting with cast iron grit. Both surfaces were blasted with #16 grit. The surface on the left was then blasted with #80 grit.

Chemical-etching can be used to roughen surfaces. In this technique, the chemical etch preferentially attacks certain crystal facets, phases or grain boundaries. Figure 2-14 shows Kovar™ which has been roughened by etching in ferric chloride.[96] A porous surface on molybdenum (and other metals) can be formed by first oxidizing the surface and then etching the oxide from the surface.[97][98] A porous material can be formed by making a 2-component alloy and then chemically etching one constituent from the material. For example, the plating-grade acrylonitrile-utadiene-styrene (ABS) copolymer is etch-roughened by a chromic-sulfuric acid etch.[99] Some glass surfaces can be made porous by selective leaching.[100] Alumina can be etched and roughened in molten (450°C) anhydrous NaOH.[101][102] Many of the etches used in the preparation of metallographic samples preferentially etch some crystallographic planes and are good roughening etches for fine-grained materials.[103]

Table 2-3. Size Specification for Cast Iron Grit (SAE J444)

Grit No.	Screen collection[a]	Screen opening		
		Screen No.	mm	inches
G10	All pass No. 7 screen	7	2.82	0.1110
	80% min. on No. 10 screen	10	2.00	0.0787
	90% min. on No.12 screen	12	1.68	0.0861
G12	All pass No. 8 screen	8	2.38	0.0937
	80% min. on No. 12 screen			
	90% min. on No. 14 screen	14	1.41	0.0555
G14	All pass No. 10 screen			
	80% min. on No. 14 screen			
	90% min. on No. 16 screen	16	1.19	0.0469
G16	All pass No. 12 screen			
	80% min. on No. 16 screen			
	90% min. on No. 18 screen	18	1.00	0.0394
G18	All pass No. 14 screen			
	75% min. on No. 18 screen			
	85% min. on No. 25 screen	25	0.711	0.0280
G25	All pass No. 16 screen			
	70% min on No. 25 screen			
	80% min. on No. 40 screen	40	0.519	0.0165
G40	All pass No. 18 screen			
	70% min. on No. 40 screen			
	80% min. on No. 50 screen	50	0.297	0.0117
G50	All pass No. 25 screen			
	65% min. on No. 50 screen			
	75% min. on No. 80 screen	80	0.18	0.0070
G80	All pass No. 40 screen			
	65% min. on No. 80 screen			
	75% min. on No. 120 screen	120	0.12	0.0040
G120	All pass No. 50 screen			
	60% min> on No. 120 screen			
	70% min. on No. 200 screen	200	0.074	0.0029
G200	All pass No. 80 screen			
	55% min. on No. 200 screen			
	65% min. on No. 325 screen	325	0.043	0.0017
G325	All pass No. 120 screen			
	20% min. on No. 325 screen			

[a]minimum cumulative percentages by weight allowed on the screens of numbers and opening size as indicated

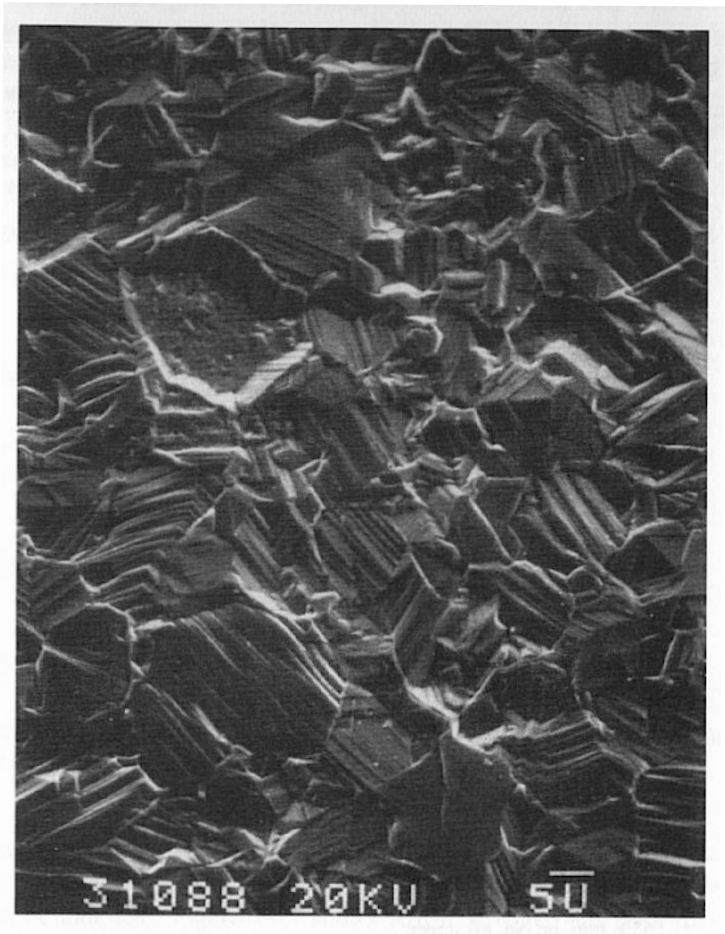


Figure 2-14. Kovar™ roughened by chemical etching with a ferric chloride solution.

Sputter-etching is a common technique for preferentially etching a surface to reveal the crystalline structure.[104] Sputtering of some crystallographic surfaces will texture the surface due to the channeling and focusing of the impinging ions and collision cascades. Surface features may be developed due to preferential sputtering of crystallographic planes. Sputtering can also be used to texture (sputter-texture) surfaces to produce very fine features with extremely high surface areas.[105] In one method of sputter texturing, the surface being sputtered is continually being coated by

a low-sputter-yield material, such as carbon, which agglomerates on the surface into islands which protect the underlying material from sputtering.[106] The result is a texture of closely spaced conical features as shown in Figure 2-15. This type of sputter texturing has been used to generate optically absorbing surfaces and to roughen surfaces of medical implants to encourage bone growth and adhesion.[107] Ultrasonic cleaning (Sec.12.4.5) can also lead to micro-roughening of metal surfaces.

Rough surfaces can also by prepared by plasma-spraying a coating of material on the substrate.[108] This technique provided a porous surface.

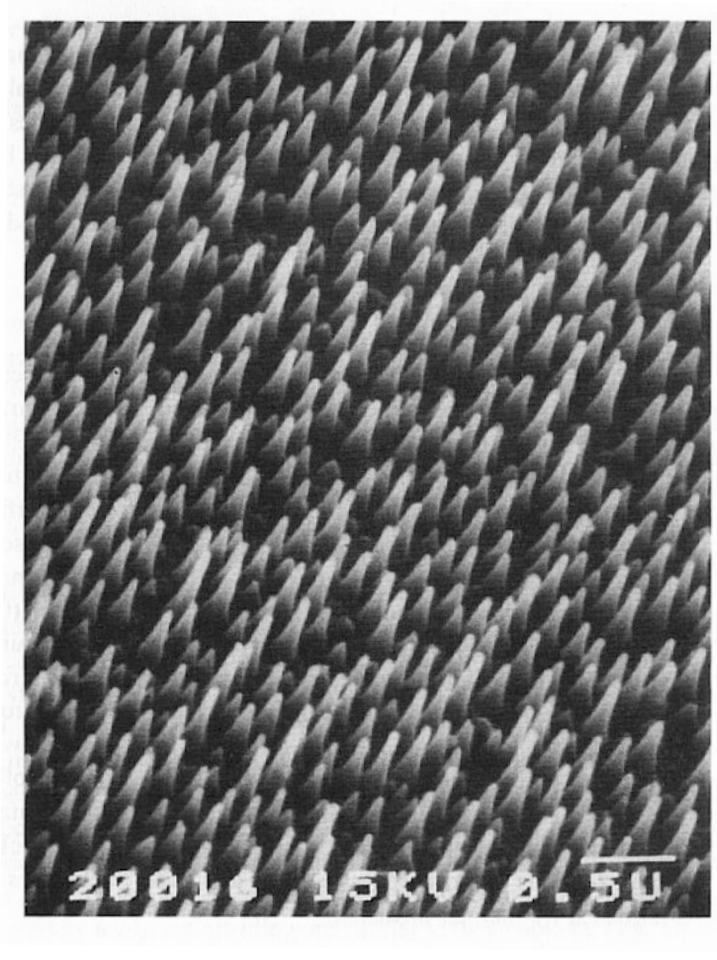


Figure 2-15. Copper roughened by sputter-etching a carbon-contaminated surface.

Vicinal (Stepped) Surfaces

Steps on Si, Ge and GaAs single crystal surfaces can be produced by cutting and polishing at an angle of several degrees to a crystal plane. This procedure produces an off-cut or vicinal surface[109] comprised of a series of closely spaced steps. These steps aid in dense nucleation for epitaxial growth of GaAs on Si[110] and $Al_xGa_{1-x}As$ on GaAs[111] by low temperature MOCVD.

2.6.2 Surface Hardness

Hardness is the resistance of a surface to elastic or plastic deformation. In many hard coating applications, the substrate must be able to sustain the load since if the surface deforms the film will be stressed, perhaps to the point of failure. Properties of hard materials have been tabulated in Ref. 112. To increase the load carrying capability the substrate surface of some materials can be hardened before the film is deposited.

Hardening by Diffusion Processes

Substrate surfaces can be hardened and dispersion strengthened by forming nitride, carbide, or boride dispersed phases in the near-surface region by thermal diffusion of a reactive species into the surface.[113][114] Steels that contain aluminum, chromium, molybdenum, vanadium or tungsten can be hardened by thermal diffusion of nitrogen into the surface. Typically nitriding is carried out at 500–550°C for 48 hours in a gaseous atmosphere giving a hardened thickness or "case depth" of several hundred microns. In carburizing, the carbon content of a low-carbon steel (0.1–0.2%) is increased to 0.65–0.8% by diffusion from a carbon-containing vapor at about 900°C. Carbonitriding can be performed on a ferrous material by diffusing both carbon and nitrogen into the surface. Nitrogen diffuses faster than the carbon so a nitrogen-rich layer is formed below the carbonitrided layer and, if quenched, increases the fatigue strength of the carbonitrided layer. Hardening by boronizing can be done on any material having a constituent that forms a stable boride such as Fe_2B, CrB_2, MoB or NiB_2. Table 2-4 lists some hardness values and case thicknesses for materials hardened by thermal diffusion.

Table 2-4. Hardening of Surfaces by Thermal Diffusion

Treatment	Substrate	Microhardness ($kg/mm^{2)}$	Case depth (microns)
Carburizing	Steel: Low C, Med C, C-Mn Cr-Mo, Ni-Mo, Ni-Cr-Mo	650-950	50-3000
Nitriding (ion)	Steel: Al, Cr, Mo, V or W (austinic stainless)	900-1300	25-750
Carbonitriding	Steel: Low C, Med C, Cr Cr-Mo, Ni-Cr-Mo	550-950	25-750
Boriding	Steel: Mo, Cr, Ti, cast Fe Cobalt-based alloys Nickel-based alloys	1600-2000	25-500

Diffusion coatings can also be formed by pack cementation.[115] In this technique, the diffusion coatings are formed by heating the surface in contact with the material to be diffused (solid state diffusion) or by heating in a reactive atmosphere which will react with the solid material to be diffused to form a volatile species which is then decomposed on the surface and diffuses into the surface (i.e. similar to Chemical Vapor Deposition—Sec. 1.1.2). Aluminum (aluminizing), silicon (siliconizing) and chromium (chromizing) are the most common materials used for pack cementation.

The use of a plasma for ion bombardment enhances the chemical reactions and diffusion[59][60] and also allows *in-situ* surface cleaning by sputtering and hydrogen reduction. The bombardment can also be the source for heating the material being treated. Typically a plasma containing NH_3, N_2 or N_2-H_2 (" forming gas"—9 parts N_2 : 1 part H_2) is used along with substrate heating to 500–600°C to nitride steel.[116] The term "Ionitriding" has been given to the plasma nitriding process.[117-119] This process is being used industrially to harden gears for heavy machinery applications. Bombardment from a nitrogen plasma can be used to plasma nitride a steel surface prior to the deposition of a TiN film.[120][121] Ion beams of nitrogen have been used to nitride steel and the structural changes obtained by ion beam nitriding are similar to those obtained by ionitriding.

Plasma carburizing is done in a carbon-containing environment.[122][123] Low temperature plasma boronizing can also be performed.[124]

Hardening by Mechanical Working

Mechanical working of a ductile surface by shot peening[125][126] or deformation introduces work hardening and compressive stress which makes the surface hard and less prone to microcracking. In shot peening, the degree of compressive stress introduced is measured by the bending of a beam shot-peened on one side (Almen test—SAE standard). Shot peening is used on high-strength materials that will be mechanically stressed, such as auto crankshafts, to increase their fatigue strength. Cold rolling may be used to increase the fatigue strength of bolts and fasteners.

Hardening by Ion Implantation

Ion implantation refers to the bombardment of a surface with high energy ions (sometimes mass and energy analyzed) whose energy is sufficient to allow significant penetration into the surface region.[127][128] Typically ion implantation uses ions having energies of 100 keV - 2 MeV which results in mean ranges in materials of up to several thousand angstroms depending on the relative masses of the bombarding and target atoms. The most commonly used ions for surface hardening are those of gaseous species, with N^+ being most often used. Typical bombardment is done at an elevated temperature (e.g. 300°C) with a bombarding dose on the order of 10^{17} cm^{-2}. The maximum concentration of implanted species is determined by sputter profiling of the surface region.[129]

Other materials can be ion implanted and are under investigation for commercial applications. These include a combination of titanium and carbon implantation which produces an amorphous surface layer at low temperatures and carbide precipitation at high temperatures.[130] Ion implantation of active species has been shown to increase the erosion and wear resistance of surfaces (Ti/C on steel, N on steel), the hardness of surfaces (Ni on Al).[131] the oxidation resistance of surfaces (Pt on Ti) and tribological properties of surfaces.[132] Ion implantation of inert species has been shown to increase the hardness of TiN films.[133][134] Ion implantation can cause a metal surface to become amorphous.[135]

In plasma immersion ion implantation (PIII) the metallic substrate is immersed in a plasma and pulsed momentarily to a high potential (50–100 kV). Ions are accelerated to the surface from the plasma and before there is a arc-breakdown, the pulse is terminated.[136]-[139] This technique has been used to carburize a substrate surface prior to deposition of a hard coating. The process is similar to ionitriding where the reaction in-depth depends on thermal diffusion. In plasma source ion implantation (PSII) the plasma is formed in a separate plasma source and a pulsed negative bias attracts the ions from the plasma to bombard and heat the surface.[140]-[142]

2.6.3 Strengthening of Surfaces

Fracture toughness is a measure of the energy necessary to propagate a crack and the strength of the surface. A high fracture toughness means that considerable energy is being absorbed in elastic and plastic deformation. Brittle materials have a low fracture toughness. Fracture toughness can be increased by having the region around the crack tip in compression. A high fracture toughness and a lack of crack initiating sites, contributes to the strength of a material.

Thermal Stressing

Materials having a high modulus, a low thermal conductivity, and a non-zero coefficient of thermal expansion, such as many glasses, can be strengthened by heating the part then rapidly cooling the surface while the interior cools slowly. This places the surface region in a compressive stress (>10,000 psi or 69 MPa) and the interior in a state of tensile stress. The material then resists fracture but if a crack propagates through the compressive surface layer the energy released results in the material fracturing into small pieces. If the compressive stress in the surface region is too high, the internal tensile stress can cause internal fracturing. In stressed glass, inclusions ("stones") in the glass can lead to spontaneous breakage after strengthening.

Thermal stressing of the substrate surface also occurs when a deposited hard coating has a different coefficient of thermal expansion (CTE) than the substrate and the deposition is done at a high temperature. If the coating has a higher CTE it shrinks more on cooling than does the

substrate, putting the coating in tensile stress and the substrate surface in compressive stress. This can result in microcracking of the coating. If the coating has a lower CTE than the substrate, the coating is put into compressive stress and the substrate into tensile stress which can produce blistering of the coating. At high temperatures, some of the hard coating materials plastically deform more easily than do others.[143] For example, at high temperatures TiC plastically deforms more easily than does TiB_2.[144]

In some cases it may be desirable to have a tough (fracture-resistant) interlayer deposited on the substrate to aid in supporting the hard coating and provide corrosion resistance. Such materials might be nickel or tantalum[145] which are typically good adhesion interlayers for metallic systems. This layer can be diffused and reacted with the substrate prior to deposition of the hardcoat.

Ion Implantation

Ion implantation of ceramic surfaces can reduce the fracturing of brittle surfaces under load[146]-[149] by the introduction of a compressive stress in the surface region both by atomic peening and by surface-region amorphization which is accompanied by a volume expansion. Amorphitizing the surface of ceramics improves their fracture resistance and provides better wear resistance, even though the surface hardness may be decreased.

Chemical Strengthening

Brittle surfaces and interfaces can be strengthened by placing them in compressive stress.[150] This can be done by stuffing the surface with larger ions (e.g. K for Na) (chemical strengthening). In cases where sharp surface flaws have decreased the fracture toughness of a surface the flaws can be blunted by chemical etching. This will increase the fracture strength of the surface. For example, after grinding a glass or ceramic surface, the surface should be etched in hydrofluoric acid which will blunt the cracks.

2.6.4 Surface Composition

Changing the surface chemistry may be advantageous in nucleating the depositing film material. The surface chemistry can be changed by

diffusing species into the surface as discussed in surface hardening. Surface composition can be changed by selective removal of a surface species. For example, bombardment of a metal carbide surface by hydrogen ions results in the decarburization of a thin surface layer producing a metallic surface on the carbide.[151] Sputtering of a compound surface often results in a surface depleted in the species having the least mass[152] or highest vapor pressure.[153] This can be an important factor in "sputter cleaning" (Sec. 12.10.2).

Inorganic Basecoats

Inorganic (non-polymer) basecoats can provide layers to aid in adhesion (adhesion layer or glue layer) of a film to a surface. For example, in the Ti-Au metallization of oxides, the titanium adhesion layer reacts with the oxide to form a good chemical bond and the gold alloys with the titanium. The layers may also be used to prevent interdiffusion (diffusion barrier) between subsequent layers and the substrate. For example, the electrically conductive compound TiN is used as a barrier layer between the aluminum metallization and the silicon in semiconductor device manufacturing. Nickel is used on brass to prevent the zinc in the brass from diffusing into the deposited film. The basecoat may also change the mechanical properties of the interface such as providing a compliant layer to modify the mechanical stresses that appear at the interface.[154] The base coat can also provide corrosion resistance when the surface layer cannot do so. Nickel, palladium-nickel (Pd-Ni), and tantalum are often used for this purpose.[154a] The Pd-(10-30%) Ni electrodeposited alloy is used as a replacement for gold in some corrosion resistant applications.[155][156] The nickel is thought to act as a grain-refiner for the electrodeposited palladium. Layered coatings of nickel and chromium are used as a diffusion barrier and for corrosion enhancement when coating TiN on brass hardware for decorative/functional applications.

Oxidation

Oxidation can be used to form oxide layers on many materials and this oxide layer can act as a diffusion barrier or electrical insulation layer between the film and the substrate. Thermal oxidation is used to form oxide layers on silicon. In furnace oxidation, the type of oxide formed can depend

on the oxygen pressure. A wet-hydrogen atmosphere may be used to oxidize some metal surfaces. Figure 2-16 shows the stability of metal oxide surfaces in a high temperature hydrogen atmosphere having varying dew points of water vapor. The dew point of the hydrogen can be adjusted by bubbling the hydrogen through water. The use of a UV/ozone environment (Sec. 12.3.4) allows the rapid oxidation of many materials at room temperature because of the presence of ozone as the oxidation agent.

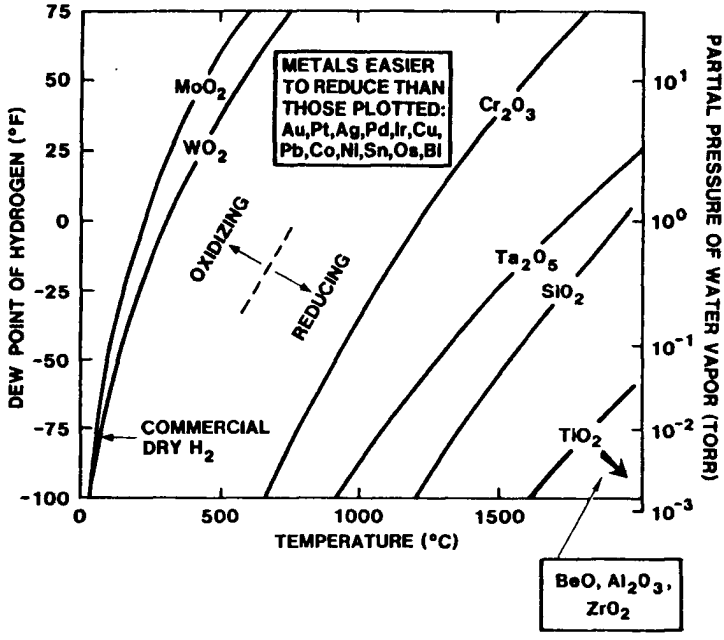


Figure 2-16. Stability of metal oxides in a hydrogen-water vapor environment.

Anodization is the electrolytic oxidation of an anodic metal surface in an electrolyte. The oxide layer can be made thick if the electrolyte continually corrodes the oxide during formation.[157][158] Barrier anodization uses borate and tartrate solutions and does not corrode the oxide layer. Barrier anodization can be used to form a very dense oxide layer on some metals ("valve" metals) including aluminum,[159][160] titanium,[161] and tantalum. The thickness of the anodized layer is dependent on the electric field giving a few Ångstroms/volt (about 30 Å/volt for aluminum). The process is very sensitive to process parameters in particular to "tramp ions" that

may cause corrosion in the bath. Anodized Ti, Ta, and Nb are used as jewelry where the oxide thickness provides colors from interference effects and the color depends on the anodization voltage. In anodic plasma oxidation, plasmas are used instead of fluid electrolytes to convert the surface to an oxide.[162]

Surface Enrichment and Depletion

Gibbs predicted that at thermodynamic equilibrium the surface composition of an alloy would be such that the surface would have the lowest possible free energy and that there would be surface enrichment of the more reactive species.[163] This means that on heating, some alloys will have a surface that is enriched in one of the component materials.[164] Heating stainless steel in an oxidizing atmosphere results in surface segregation of chromium which oxidizes and provides the corrosion protection.[165] Aluminum-containing steel, beryllium containing copper (copper beryllium alloy), and silver - 1%Be have surface segregation of the aluminum or beryllium in an oxidizing atmosphere.

Leaching is the chemical dissolution (etching) of a material or of a component of a material. The leaching of metal alloy surfaces can lead to surface enrichment of the materials that are less likely to be leached. Leaching was used by the Pre-Columbian Indians to produce a gold surface to an object made of a low-gold-content copper alloy. The copper alloy object was treated with mineral acid (wet manure) which leached the copper from the surface leaving a porous gold surface which was then buffed to densify the surface and produces a high-gold alloy appearance.[166]

Phase Composition

In the growth of epitaxial films the crystallographic orientation and lattice spacing of the surface can be important. Typically the lattice mismatch should only be several percent in order that interfacial dislocations do not cause a polycrystalline film to form. A graded buffer layer may be used on the surface to provide the appropriate lattice spacing. For example, thick single crystal SiC layers may be grown on silicon by CVD techniques although the lattice mismatch between silicon and silicon carbide is large (20%).[167] This is accomplished by forming a buffer layer by

first carbonizing the silicon surface and then grading the carbide composition from the substrate to the film.

2.6.5 Surface "Activation"

Activation is the temporary increase of the chemical reactivity of the surface, usually by changing the surface chemistry. The effect of many surface treatments on polymers will degrade with time. Treatment of polymers with unstable surfaces, such as polypropylene where the material is above its glass transition temperature at room temperature, or polymers containing low molecular-weight fractions, such as plasticizers, will degrade the most rapidly. The activated surface should be used within a specified time period after activation.

Plasma Activation

Plasma treatment of polymer surfaces with inert or reactive gases can be used to activate polymer surfaces[168]-[172] either as a separate process or in the PVD chamber. Generally oxygen or nitrogen plasmas are used for activating the surfaces. For example, ABS plastic is oxygen plasma treated before a decorative coating of a chromium alloy (80%Cr : 15% Fe : 5%Ti) is sputter deposited on decorative trim in the automotive industry. In general, oxygen plasma treatment makes the surfaces more acidic owing to the formation of carbonyl groups (C=O) on the surface. Nitrogen or ammonia plasma treatments make the surfaces more basic, owing to the "grafting" of amine and imine groups to the surface.[173]-[176] Surfaces can be over-treated with plasmas creating a weakened near-surface region and thus reduced film adhesion. Oxygen plasma treatment of carbon increases the acidity of the surface by oxidation.[177]

Surfaces can be treated in inert gas plasmas. In the early studies of plasma treatment with inert plasmas ("CASING"—Crosslinking by Activated Species of Inert Gas)[178][179] plasma contamination probably resulted in oxidation. The activation that does occur in an inert gas plasma is probably from ultraviolet radiation from the plasma causing bond scission in polymers or the generation of electronic charge sites in ceramics.[180]

Plasma treatment of polymer surfaces can result in surface texturing and the improved adhesion strengths can then be attributed to mechanical

interlocking. This texturing may be accompanied by changes in the surface chemistry due to changes in the termination species.[181]

Plasma treatment equipment can have the substrate in the plasma generation region or in a remote location. A common configuration is when the substrate is placed on the driven electrode in a parallel plate rf plasma system such as is shown in Fig. 1-2. When plasma treating a surface, it is important that the plasma be uniform over the surface. If these conditions are not met, non-uniform treatment can occur. This is particularly important in the rf system where if an insulating substrate does not completely cover the driven electrode, the treatment action is "shorted out" by the regions where the plasma is in contact with the metal electrode. To overcome this problem, a mask should be made of a dielectric material that completely covers the electrode with cut-outs for the substrates.*

Corona Activation

Polymer surfaces can be altered by corona treatments. A corona discharge is established in ambient pressure air when a high voltage/high frequency potential is applied between two electrodes, one of which has a coating of material with a dielectric constant greater than air.[182]-[186] If the surfaces have a dielectric constant less than air or if there are pinholes in the coating, spark discharges occur. The surface to be treated is generally a film that is passed over the electrode surface (usually a roller). The corona creates activated oxygen species that react with the polymer surface breaking the polymer chains, reacting with the free radicals and creating polar functional groups thus giving higher energy surfaces. The corona discharge is commonly used on-line to increase the surface energy of polymer films so as to increase their bondability and wettability for inks and adhesives.[187] The corona treatment can produce microroughening of the surface which may be undesirable.[188]

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*A person was treating a polymer container with an oxygen plasma to increase its wettability and found that the treatment was not uniform over the surface. The polymer substrate was not covering the whole electrode surface and the edges of the container were being treated whereas the center was not. A holder of the polymer material was made that covered the whole electrode with cutouts for the containers and then the treatment was uniform.

Flame Activation

Flame activation of polymer surfaces is accomplished with an oxidizing flame.[187][189][190] In the flame, reactive species are formed which react with the polymer surface creating a high surface energy. The surface activation is not as great as with corona treatments but does not decrease as rapidly with time as does the corona treatment. This treatment is often used in "off-line" treatment of polymers for ink printing.

Electronic Charge Sites and Dangling Bonds

Activation of a surface can be accomplished by making the surface more reactive without changing its composition. This is often done by generating electronic charge sites in glasses and ceramics or bond scission that create "dangling bonds" in polymers. Activation of polymer surfaces can be accomplished using UV, x-ray,[191] electron, or ion[180][192][193] irradiation. These treatments may provide reactive sites for depositing adatoms or they may provide sites which react with oxygen which then act as the reactive site. The acidity (electron donicity) of oxide surfaces can be modified by plasma treatment apparently by creation of donor or acceptor sites. For example, the surface of ammonia-plasma-treated TiO_2 shows an appreciable increase in acidity.[194] In depositing aluminum films on Kapton™ the best surface treatment for the Kapton™ was found to be a detergent clean followed by a caustic etch to roughen the surface and then UV treatment in a partial pressure of oxygen which oxidized the surface.

Activation of ionically bonded solids may be by exposure to electron, photon, or ion radiation which creates point defects. Electron and photon radiation of insulator and semiconductor surfaces prior to film deposition have been used to enhance the adhesion of the film,[195] probably by generating charge sites and changing the nucleation behavior of the adatoms.

Ion bombardment of a surface damages the surface[196] and may increase the reactivity of the surface.[197][198] It is proposed that the generation of lattice defects in the surface is the mechanism by which reactivity is increased. This surface reactivity increases the nucleation density of adatoms on the surface.

UV/O_3 exposure has also been shown to promote the adsorption of oxygen on Al_2O_3 surfaces[199] and this may promote nucleation on the surface and subsequent good adhesion of films to the surface. This

adsorbed material is lost from the surface in a time-dependent manner and so the exposed surface should be coated as quickly as possible.

Activation of a polymer surface can be done by the addition of an evaporated or plasma deposition of a polymer film that has available bonding sites.[200]

Surface Layer Removal

The removal of the oxide layer from metal surfaces is an activation process if the surface is used before the oxide reforms. In electroplating, the oxide layer can be removed by chemical or electrolytic treatments just prior to insertion into the electroplating bath. Such activation is used for plating nickel-on-nickel, chrome-on-chrome, gold-on-nickel, silver-on-nickel, and nickel-on-Kovar™. For example, acid cleaning of nickel can be accomplished by immersion of the nickel surface into an acid bath (20 pct by volume sulfuric acid) followed by rapid transferring through the rinse into the deposition tank. The part is kept wet at all times to minimize re-oxidation.

Mechanical brushing or mechanical activation, of metal surfaces just prior to film deposition is a technique that produces improved adhesion of vacuum deposited coatings on strip steel.[201] The mechanical brushing disrupts the oxide layer, exposing a clean metal surface.

2.6.6 Surface "Sensitization"

"Sensitization" of a surface is the addition of a small amount of material to the surface to act as nucleation sites for adatom nucleation. This may be less than a monolayer of material. For example, one of the "secrets" for preparing a glass surface for silvering by chemical means is to nucleate the surface using a hot acidic (HCl) stannous chloride solution or by vigorous swabbing with a saturated solution of $SnCl_2$ leaving a small amount of tin on the surface. A small amount of tin is also to be found on the tin-contacting side of float glass. This tin-side behaves differently than the side which was not in contact with the molten tin in the float glass fabrication. Glass surfaces can be sensitized for gold deposition either by scrubbing with chalk ($CaCO_3$) which embeds calcium into the surface or by the evaporation of a small amount of Bi_2O_{3-x} (from Bi_2O_3) just prior to the gold deposition. ZnO serves as a good nucleating agent for silver films but not for gold films.

Various materials can be used as a "coupling agent" between a surface and a deposited metal film. These coupling agents may have thicknesses on the order of a monolayer. For example, sulfur-containing organic monolayers have been used to increase the adhesion of gold to a silicon oxide surface.[202][203]

Surfaces can be sensitized by introducing foreign atoms into the surface by ion implantation. For example, gold implantation has been used to nucleate silver deposition on silicon dioxide films.[204]

2.7 SUMMARY

The substrate surface and its properties are often critical to the film formation process. The substrate surface should be characterized to the extent necessary to obtain a reproducible film. Care must be taken that the surface properties are not changed by cleaning processes nor recontamination, either outside the deposition system or inside the deposition system during processing. There are a variety of ways to modify the substrate surface in order for it to provide a surface more conducive to fabricating a film with the desired properties or to obtain a reproducible surface. The substrate surface, which becomes part of the interfacial region after film deposition, is often critical to obtaining good adhesion of the film to the substrate.

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3

The Low-Pressure Gas and Vacuum Processing Environment

3.1 INTRODUCTION

PVD processing is done in a low pressure gaseous (vacuum) environment. This low pressure environment provides a long mean free path for collision between the vaporization source and the substrate. It also allows control of the amount of gaseous and vapor contamination during processing. The vacuum environment is generated by a vacuum system which includes the deposition chamber, introduction chambers ("load-lock chambers") if used, the vacuum pumping system ("pumping stack"), the exhaust system, gas inlet system, and associated plumbing. In addition the fixturing and tooling used to hold, position, and move the substrates are important to the system design. Materials cleaned outside the deposition system can be recontaminated in the system during evacuation ("pumpdown") by "system-related contamination." During deposition, the film can be contaminated by system-related contamination and by "process-related contamination." The goal of good vacuum system design, construction, operation, and maintenance is to control these sources of contamination.

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3.2 GASES AND VAPORS

A gas is defined as a state of matter where the atoms and molecules that compose the material uniformly fill the container holding the material. Examples are the atomic gases of helium, neon, argon, krypton and xenon and the molecular gases of hydrogen, nitrogen, and oxygen. A vapor can be defined as a gaseous species which can be easily condensed or adsorbed on surfaces; examples include water vapor, plasticizers (e.g. pthlates) from molded polymers, many solvents, and zinc vapors from hot brass. Often a vapor molecule is larger than a gas molecule. For example, the water molecule (H-O-H) has a triangular configuration with an effective molecular diameter of 13Å compared to a molecular diameter of 2.98Å for oxygen (O-O) and 2.40Å for hydrogen (H-H). A gas or vapor is characterized by its atomic or molecular weight, and number density expressed as atoms or molecules per cubic centimeter. The atomic or molecular weight is measured in atomic mass units (amu). The atomic mass unit is defined as $^1/_{12}$ of the mass of the C^{12} isotope; i.e. = 1.66×10^{-24} g. Table 3-1 lists the atomic masses of some common gases and vapors.

Table 3-1. Atomic and Molecular Mass of Some Gases and Vapors (amu)

Hydrogen atom (H)	1	Nitrogen (N_2) & Carbon monoxide (CO) molecule	28
Hydrogen molecule (H_2)	2	Carbon dioxide molecule (CO_2)	44
Helium atom (He)	4	Argon atom (Ar)	40
Oxygen molecule (O_2)	32	Krypton atom (Kr)	80
Hydroxyl radical (OH^-)	17	Xenon atom (Xe)	130
Water molecule (H_2O)	18	Mercury atom (Hg)	200

Avogadro's number is the number of molecules in a mole* of the material and is equal to 6.023×10^{23}. Under "standard temperature and pressure" (STP) conditions of 0°C and 760 Torr, a mole of gas occupies

*A mole is the gram-molecular-weight of a material. For example, argon has a molecular weight of 39.944, and 39.944 grams of argon will be one mole of the gas.

22.4 liters of volume. In a standard cubic centimeter (scc) of a gas, there are 2.69 x 10^{19} molecules.

A "vacuum" is a condition where the gas pressure in a container is less than that of the ambient pressure. The pressure difference can be small, such as that used to control gas flow in the system or large such as that used in PVD systems to give a long mean free path for vaporized particles and to allow the control of gaseous and vapor contamination to any desired level. A "rough" vacuum (10^{-3} Torr) is one having a pressure about 10^{-6} of that of the atmosphere or about 10^{13} molecules/cm^3. A "good" vacuum (10^{-6} Torr) has a pressure of about 10^{-9} that of atmosphere or 10^{10} molecules/cm^3. In a very-ultrahigh vacuum (VUHV-10^{-12} Torr) there are about 10^4 molecules per cubic centimeter.

3.2.1 Gas Pressure and Partial Pressure

The molecules in a gas have a kinetic energy of $^1/_2\ mv^2$ where m is the mass and v is the velocity or equal to $^3/_2\ kT$ where k is Boltzmann's constant and T is the temperature in degrees Kelvin. At room temperature $^3/_2\ kT$ equals 0.025 ($^1/_{40}$) eV. When these molecules strike a surface, they exert a pressure which is measured as force per unit area. The pressure exerted at a given temperature and gas density, depends on the atomic/ molecular weight of the gas molecules. The pressure is the sum of the forces exerted by all particles impinging on the surface, If there is a mixture of gases or of gases and vapors, then each gas or vapor will exert a partial pressure and the total pressure will be the sum of their partial pressures. Molecular energies can also be described by their "temperature" which is determined by their kinetic energy.

The ambient pressure is the pressure at a specific location and varies with location, temperature, and weather. There are a number of pressure units in use around the world. Table 3-2 gives the conversion from one to another. A standard of pressure is the Standard Atmosphere which at 0°C, and sea level, is:

1.013 x 10^5 Newtons/m^2 or Pascals (Pa) or 14.696 pounds/in^2 (psi) or 760 mm Hg (Torr)

The pressure in Pascal (Pa) = 133.3 x P (in Torr) or Pa = 0.1333 x P (in mTorr). The milliTorr (mTorr = 10^{-3} Torr) or micron is a pressure unit often used in vacuum and plasma technology.

Table 3-2. Conversion of Pressure Units

	Pa	bar	mbar	atm	Torr	mTorr	psi
1 Pa =1 N/m^2	1	10^{-5}	10^{-2}	$9.8692x10^{-6}$	$750.06x10^{-5}$	7.5	$1.4504x10^{-4}$
1 bar =0.1 MPa	10^5	1	10^3	0.98692	750.06	$7.5x10^5$	14.5032
1 mbar = 10^2 Pa	10^2	10^{-3}	1	$9.8692x10^{-4}$	0.75006	750	$14.5032x10^{-3}$
1 atm = 760 Torr	101325	1.013	1013.25	1	760	$7.6x10^5$	14.6972
1 Torr = 1 mm Hg	133.322	[3]0.00133	1.333	$1.3158x10^{-3}$	1	103	0.01934
1 mTorr = 0.001 mm Hg	0.133	$1.3x10^{-6}$	0.00133	$1.3x10^{-6}$	10^{-3}	1	$1.9x10^{-5}$
1 psi	6894.8	0.06895	68.95	0.06804	51.715	$5.1x10^4$	1

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Pressure Measurement

The gas pressure can be monitored directly and indirectly by use of vacuum gauges.[1] The output of the vacuum gauges is often used to control various aspects of PVD processing such as when to "crossover" from roughing to high vacuum pumping and when to begin thermal evaporation. Vacuum gauges can function by several methods including:

- *Pressure exerted on a surface with respect to a reference*—e.g. support of a column of liquid as in a mercury manometer; deflection of a diaphragm as in a capacitance manometer gauge.[2]
- *Thermal conductivity of gas*—e.g. thermocouple gauge; Piriani gauge.[3]
- *Ionization and collection of ions*—e.g. hot cathode ionization gauge;[4][5] cold cathode ionization gauge; radioactive ionization source gauge.
- *Viscosity measurement (i.e. molecular drag)*—e.g. spinning rotor gauge.[6]
- *Ionization with mass analysis and peak-height calibration*—e.g. mass spectrometer.

Figure 3-1 shows some gauge configurations. These pressure measurement techniques, except for mass spectrometry, do not define the gaseous species nor their chemical state (atoms, molecules, radicals, ions, excited species). They require calibration in order to provide a molecular density measurement. Table 3-3 lists some pressure ranges and the best accuracy of gauges commonly used in PVD processing.*[7]

Vacuum gauge placement is important in establishing a reproducible process and the placement of vacuum gauging is important in system design. Vacuum gauges can only measure their surrounding environment.

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*It seems to be fairly common that people try to control the pressure in the 2–5 mTorr range for sputtering with a thermocouple gauge or piriani gauge. These gauges do not have the sensitivty that you should have for reproducible processing when used in that pressure range. The properties of low-pressure sputter-deposited films are very sensitive to the gas pressure during sputtering because of the concurrent bombardment from reflected high energy neutrals (Sect. 9.4.3).

If the gauge is in a side tube it may not be measuring the real processing environment. "Nude" gauges are made to be inserted into the processing chamber but they may be degraded by the processing. Gauge placement is to some degree dictated by whether the gauges are used to measure an absolute pressure value or are to be used to establish reproducible processing conditions by measuring relative pressure values. Often reference gauges are placed on the same system as the working gauge. A valving system allows *in situ* comparison of the gauges to detect gauge drift in the working gauge.

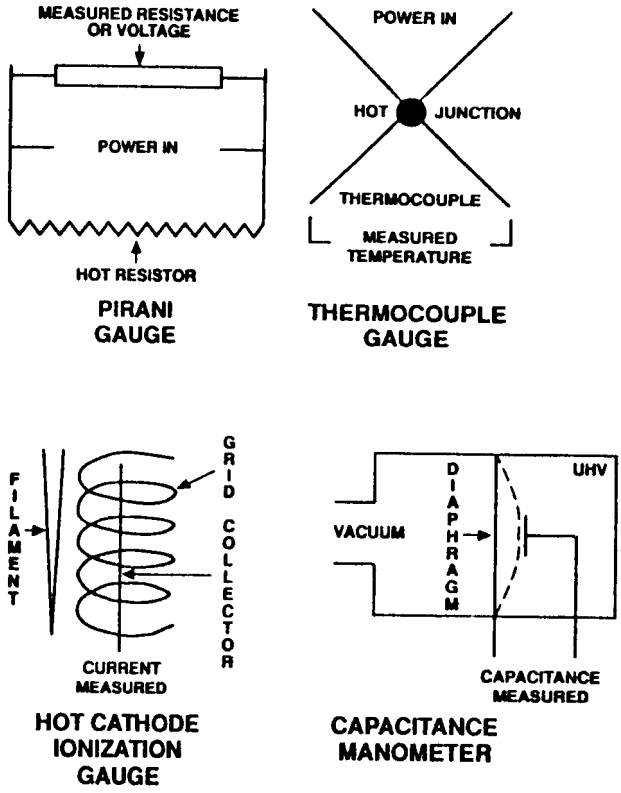


Figure 3-1. Vacuum gauge configurations.

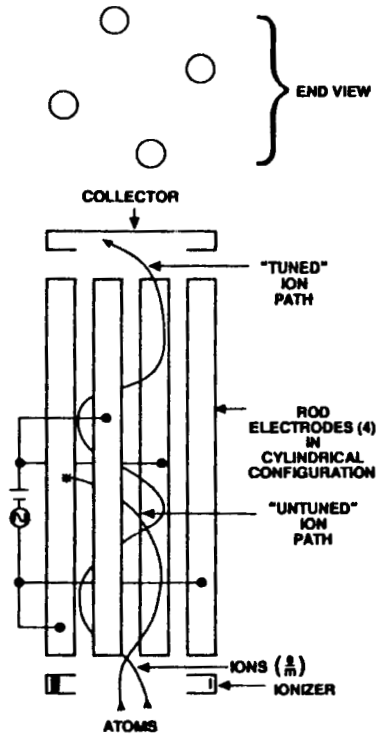


Figure 3-1 cont. A quadrapole mass spectrometer.

Table 3-3. Pressure Ranges of Various Vacuum Gauges[7]

Gauge type	Pressure range (Torr)	Accuracy
Capacitance diaphragm (CDG)	atmosphere to 10^{-6}	±0.02 to 0.2%
Thermal conductivity (Piriani)	atmosphere to 10^{-4}	±5%
Hot cathode ionization (HCIG)	10^{-1} to 10^{-9}	±1%
Viscosity (spinning rotor)	1 to 10^{-8}	±1 to 10%

Some rules about gauge placement are:

- Gauges should be placed as close to the processing volume as possible.
- Gauges should not be placed near pumping ports or gas inlet ports. They particularly should not be placed in the "throat" of the high vacuum pumping stack.
- Gauges should not be placed in line-of-sight of gas inlet ports since they then behave as "arrival rate transducers."
- Gauges should be placed so that they are not easily contaminated by backstreaming, e.g. heated filaments "crack" oils producing a carbonaceous deposit which changes the electron emission and thus the gauge calibration.
- Gauges should be placed so that they do not accumulate debris.
- Redundant gauging or gauges with overlapping ranges, should be used so that if a gauge drifts or begins to give inaccurate readings then the gauge is immediately suspect and not the system.
- In some cases it may be desirable to have gauging that is only used during pumpdown and can be isolated during processing to prevent degradation.

In some cases film properties are very sensitive to the gas pressure in the deposition environment. For example, in magnetron sputter deposited molybdenum films, the residual film stress is very sensitive to the sputtering gas pressure during sputter deposition and changes of a few mTorr can give drastic changes in the film stress (Sec. 9.4.3). In order to have process reproducibility with time, gauges should be precise and not be subject to rapid or extreme calibration changing with time ("drift"). If the vacuum gauging is to be used for process specification the gauges should be accurate (i.e. calibrated). Some gauges are more subject to

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Precision is the ability to give the same reading repeatedly even though the reading may be inaccurate. **Accuracy** is the ability to give a reading that is correct when compared to a primary (absolute) standard.

calibration drift than are others. For example, cold cathode ionization gauges are typically much more prone to drift than are hot filament ionization gauges. All vacuum gauges need periodic calibration either to a primary standard.[8] or to a secondary standard that is acceptable for the processing being used. Each gauge should have a calibration log.

Identification of Gaseous Species

The gas species in a processing chamber is determined using a mass spectrometer ("mass spec"). Figure 3-1 shows a quadrapole mass spectrometer, which is the most commonly used mass spectrometer. Another type is the magnetic sector mass spectrometer. The mass spectrometer can either have its detector in or connected directly to the processing chamber, or it can be in a differentially pumped analytical chamber when the processing chamber pressure is too high ($>10^{-4}$ Torr) for good sensitivity. In the mass spectrometer, the gas atoms and molecules are ionized, accelerated, and the charge/mass ratio analyzed in an RF field and collected in an ion collector such as a Faraday cup.

Ionization often fragments larger molecules. The charge-to-mass spectra of the fragments of the original molecule, which is called the cracking pattern, can be very complex. By calibration of the "peak height" of the signal for a particular gas species using calibrated leaks,[9] absolute values for the partial pressures of specific gases can be obtained. When used to analyze the residual gas in a vacuum chamber, the mass spectrometer is called a Residual Gas Analyzer (RGA).[10] Mass spectrometers have difficulty in measuring condensable species which can condense on surfaces and not reach the ionizer. These species can often be detected by analyzing collector surfaces placed in the system. The presence of oil contamination can be detected using contact angle measurements or the collected material can be identified using IR spectroscopy. For example, to detect oil coming from the roughing line, a clean glass slide or KBr window can be placed in front of the roughing port. The system is pumped down, returned to the ambient pressure and the material that has been collected on the surface is analyzed.

A very good RGA can detect a minimum partial pressure of N_2 to about 10^{-14} Torr. In order to identify fractions of heavy molecular species, such as pump oils, a mass spectrometer should be capable of measuring masses to the 150–200 amu range. Isotopes of atoms result in there being several RGA peaks for many species due to the differences in masses. The

RGA can be integrated with a personal computer to be used as a process monitor.[10]

3.2.2 Molecular Motion

Molecular Velocity

Gas molecules at low pressure and in thermal equilibrium, have a distribution of velocities which can be represented by the Maxwell-Boltzmann distribution. The mean speed (velocity) of molecules in the gas is proportional to $(T/M)^{1/2}$ where T is the Kelvin temperature and M is the molecular weight. At room temperature the average "air molecule" has a velocity of about 4.6 x 10^4 cm/sec, while an electron has a velocity of about 10^7 cm/sec.

Mean Free Path

The mean free path is the average distance traveled by the gas molecules between collisions and is proportional to T/P where P is the pressure. For example, in nitrogen at 20°C and 1 mTorr pressure, a molecule has a mean free path of about 5 cm.

Figure 3-2 shows the mean free path of a molecule, the impingement rate (molecules/cm^2/sec at 25°C) and the time to form one monolayer of adsorbed species (assuming a unity sticking coefficient) at room temperature as a function of pressure. It can be seen that for a pressure of 10^{-6} Torr which is a "good" vacuum, the mean free path is about five meters and the time to form one monolayer of gas is about 1 sec.

Collision Frequency

The collision frequency for an atom in the gas is proportional to $P/(MT)^{1/2}$. For example, argon at 20°C and 1 mTorr pressure has a collision frequency of 6.7 x 10^3 collisions/sec.

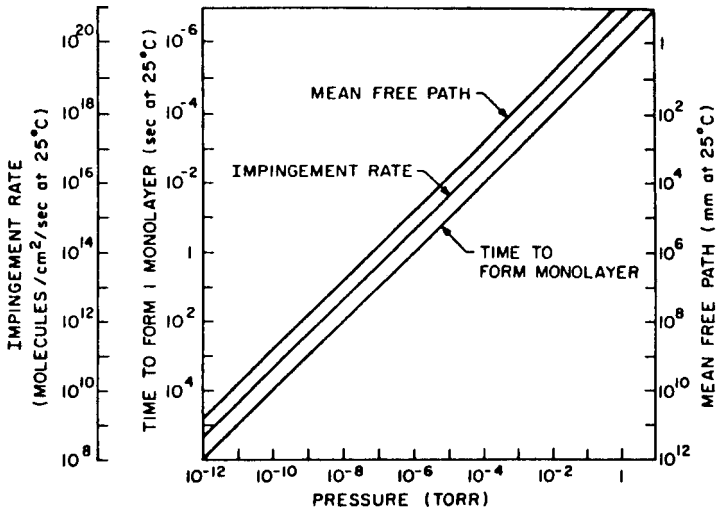


Figure 3-2. Mean free path, impingement rate and time to form a monolayer as a function of gas pressure at 25°C.

Energy Transfer from Collision and "Thermalization"

The Ideal Gas model utilizes the concept of a collision diameter, D_0, which is the distance between the centers of the spheres. When there is a physical collision D_0^2 is the collision crossection. Figure 3-3 shows the collision of two spheres (i = incident, t = target) of different masses.

From the Laws of Conservation of Energy and the Conservation of Momentum the energy, E, transferred by the collision is given by:

Eq. (1) $$E_t/E_i = 4\, M_t M_i \cos^2\theta/(M_i + M_t)^2$$

where E = energy, M = mass and the angle is as shown in Fig. 3-3. The maximum energy transfer occurs when $M_i = M_t$ and the motion is along a path joining the centers (i.e. $\theta = 0$).

When an energetic molecule passes through a gas, it is scattered and loses energy by collisions and becomes "thermalized" to the ambient energy of the gas molecules. The distance that the energetic molecule travels and the number of collisions that it must make to become thermalized depends on its energy, the relative masses of the molecules, gas pressure, and the gas temperature.[12]-[15] Figure 3-4 shows the mean free path for thermalization of energetic molecules in argon as a function of

mass and energy. This thermalization process is important in sputter deposition and in bombardment of the substrate surfaces by reflected high energy neutrals in the sputtering process. Scattering during the collisions can randomize the direction of the incident vapor flux in PVD processes.

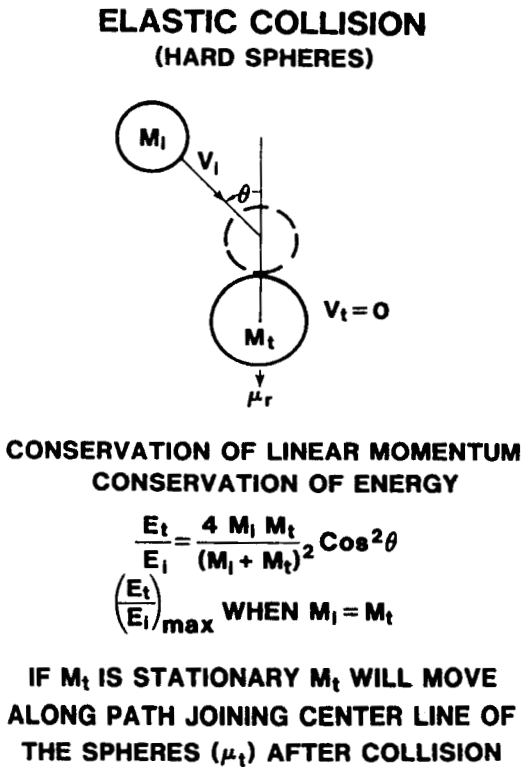


Figure 3-3. Collision of particles.

3.2.3 Gas Flow

When the mean free path of the gas molecules is short, there is appreciable internal friction and the gas flow is called viscous flow. If vortex motion is present, the viscous flow is called turbulent flow. If turbulence is not present, the viscous flow is called laminar flow. With viscous flow, the geometry of the system is relatively unimportant since the mean free path for collision is short. When the gas flow is viscous there

are many gas collisions and flow against the pressure differential ("counterflow") in a pumping system, which is called backstreaming, is minimal.[16]

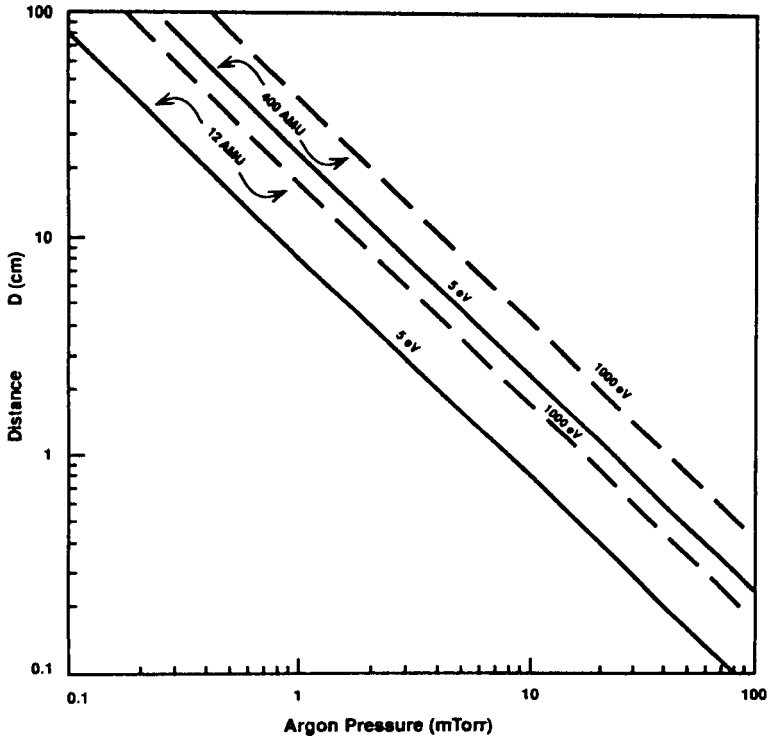


Figure 3-4. Distance traveled before thermalization by collision of heavy and light particles as a function of argon gas pressure (adapted from Ref. 12).

When the mean free path for collision is long, the molecules move independently of each other and the flow is called molecular flow. In molecular flow conditions, backstreaming can be appreciable. All oil sealed and oil vapor vacuum pumps show some degree of backstreaming[16] which contributes to surface contamination in the deposition system. Knudsen flow is the transition region between viscous flow and molecular flow regimes.

When gas flows over a surface there is frictional drag on the surface which produces a velocity gradient near the surface. This frictional drag reduces flow of fluids on the surface in a direction counter to the gas

flow (wall creep). This frictional drag is also used in the molecular drag pump to give gas molecules a directional flow.

Gas flow can be measured in standard cubic centimeters per minute (sccm) or standard cubic centimeters per second (sccs) where the standard cubic centimeter of gas is the gas at standard atmospheric pressure and 0°C. The flow can also be measured in Torr-liters/sec. For a standard atmosphere (760 Torr, 0°C) there are 2.69 x 10^{19} molecules per cubic centimeter and a Torr-liter/sec of flow is equivalent to 3.5 x 10^{19} molecules per sec. In vacuum pumping, the gas flow through the pump is called the pump throughput [Torr-l/s, ft^3(STP)/h, cm^3(STD)/s].

3.2.4 Ideal Gas Law

For a low pressure gas where there is little molecule-molecule interaction, the gas pressure and volume as a function of temperature is given by the Ideal Gas Law.

The Ideal Gas Law states that the pressure (P) times the volume (V) divided by the absolute temperature (T) equals a constant.

Eq. (2) PV/T = constant

A process performed at a constant pressure is called an isobaric process. A process performed at constant temperature is called an isothermal process. An adiabatic process is one in which there is no energy lost or gained by the gas from external sources including the container walls. The Ideal Gas Law states that in an adiabatic process in which the temperature remains constant, any change in the volume will result in a change in the pressure or $P_1V_1 = P_2V_2$ (Boyles' Law). For example if the volume is doubled then the pressure will be decreased by one half. Since the temperature is constant and the particle energy is unchanged, this means that the particle density has been reduced by half. The Ideal Gas Law also says that in an adiabatic process, if the volume is held constant and the temperature is increased the pressure will increase (Charles' Law). For example if the temperature is doubled (say from 273 K or 0°C to 546 K or 273°C) the pressure will double.

Of course no process is completely adiabatic, so when the pressure in a vacuum chamber is decreased rapidly, the gas and vapors will cool and this in turn will cool the chamber walls by removing heat from the surfaces and this prevents the gas temperature from going as low as the

Ideal Gas Law predicts. When the gas is compressed the gas temperature will rise and the walls of the container will be heated.

Heating of the gas by compression can pose problems. For example, blower pumps compress large amounts of gas and generate a lot of heat. If the blower pump is exhausted to atmospheric pressure, the pump will overheat and the bearings will suffer. Generally a blower pump is "backed" by an oil-sealed mechanical pump so that it exhausts to a pressure lower than atmospheric pressure.

3.2.5 Vapor Pressure and Condensation

The equilibrium vapor pressure of a material is the partial pressure of the material in a closed container. At the surface as many atoms/molecules are returning to the surface as are leaving the surface, and the pressure is in equilibrium. This vapor pressure is also called the saturation vapor pressure (or dew point in the case of water) since if the vapor pressure becomes higher than this value, some of the vapor will condense. Table 3-4 lists the equilibrium vapor pressure of water as a function of temperature. The boiling point is when the vapor pressure equals the ambient pressure. For water this is 100°C at 760 Torr. At about 22°C (room temperature) the equilibrium vapor pressure of water is about 20 Torr. It is important to note that vaporizing species leave the surface with a cosine distribution of the molecular flux as shown in Fig. 3-5. This means that most of the molecules leave normal to the surface.

Table 3-4. Equilibrium Vapor Pressure of Water

Temperature (°C)	Vapor pressure (Torr)
-183	1.4×10^{-22}
-100	1.1×10^{-5}
0	4.58
20	17.54
50	92.5
100	760
250	29,817

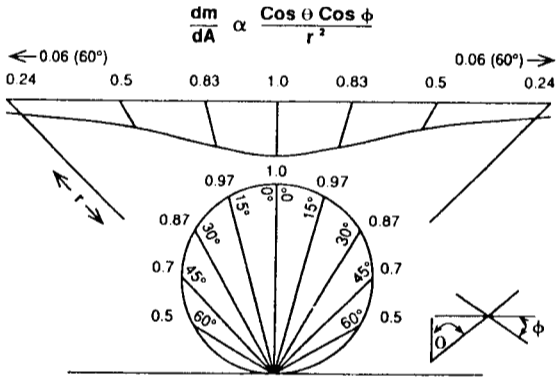


Figure 3-5. Cosine distribution of particles leaving a point on a surface.

If water vapor is cooled below its dew point without condensation, the vapor is considered supersaturated and droplet nucleation can occur on suspended particles and ions in the gas. This can be a source of contamination in a PVD system. For example, if the water vapor in the chamber is near saturation (high relative humidity), rapid evacuation and cooling can raise the relative humidity above saturation and water vapor will condense on ions and airborne particles in the system producing water droplets which will deposit on surfaces leaving a residue, (i.e. it can rain in your vacuum system).[17]-[21] The electrically charged droplets thus formed can be controlled by electrical fields in the deposition chamber to some extent.[22] In order to reduce the production of droplets due to supersaturation condensation, the system should be filled or flushed with dry gas prior to pumping, or the pumping rate should be controlled to prevent cooling to supersaturation. This slow pumping is called "soft pumping."[23][24]

Conversely if the gas/vapor is compressed, the partial pressure of the vapor will increase. If the vapor pressure exceeds the saturation vapor pressure the vapor will condense (i.e. liquefaction by compression). For example, water has a saturation vapor pressure of about 20 Torr at room temperature and if the water vapor pressure exceeds this value at room temperature some water will condense. Several types of vacuum pumps compress gases and vapors; these types of pumps are susceptible to condensing vapors and thereby lose

their ability to pump gases. For example, if an oil-sealed mechanical pump condenses water during compression, the water will mix with the oil and the oil-seal will not be effective.* Often, just changing the oil in the pump will restore the pumping efficiency of the pump. To prevent liquefaction by compression in such a pump, the vapor flowing into the pump is diluted with a dry gas (ballasted) to the extent that its partial pressure never exceeds the saturation vapor pressure during compression. This increases the pumping load on the system and should be avoided if possible.

Surfaces which are porous or have small cracks can condense vapors by capillary condensation in the "cracks."[25] This leads to condensation of liquids in capillaries, cracks, and pores even when the vapor pressure is below saturation over a smooth surface. This, together with the fact that the molecules vaporizing in the pore quickly strike a surface, makes volatilization of a liquid from a capillary much more difficult than from a smooth surface.

3.3 GAS-SURFACE INTERACTIONS

3.3.1 Residence Time

Non-reactive gas atoms or molecules bounce off a surface with a contact time (residence time) of about 10^{-12} seconds. Vapors have an appreciable residence time that depends on the temperature and chemical bonding to the surface. Table 3-5 shows the calculated residence time of some gases and vapors on surfaces at various temperatures.

Water vapor is an example of a material that has an appreciable residence time. This makes removal of water vapor from a system depend on the number of surface collisions that it must suffer before being removed. Figure 3-6 shows the partial pressures of water vapor, as a function of pumping time, that might be expected in a system if you start with wet

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*When traveling in the backcountry of Mexico we forded a deep river. Shortly thereafter we lost all power to the wheels. We discovered that when we made the river crossing, the automatic transmission was cooled rapidly and sucked water into the transmission. When the water mixed with the transmission oil, the oil frothed and lost its viscosity. We had to drain the oil from the transmission and boil it over a campstove to get the water out and then put it back in the transmission.

surfaces and with dry surfaces. Note the time scale is in hours. The result of this residence time is that removal of water vapor from a system is much slower than removal of a gaseous material such as nitrogen. Thus the contamination in many vacuum systems, under processing conditions is dominated by water vapor.

The sticking coefficient is defined as the ratio of the number of molecules that stay on a surface to the number of molecules incident of the surface. The sticking coefficient is generally temperature dependent and depends on the chemical reaction between the atoms/molecules. A material may have a sticking coefficient of less than one, meaning that statistically it must take several collisions with a surface for an atom/molecule of the material to condense. For example, molecular oxygen is much less chemically reactive than atomic oxygen and it may take several collisions with a clean metal surface to form an oxide bond, whereas the oxygen atom will form a chemical bond on the first contact. The sticking coefficient may also depend on the amount of material already on the surface i.e. the surface coverage from prior collisions.

Table 3-5. Residence Times of Gases and Vapors on Various Surfaces

System	Desorption Energy	Residence time (calculated) 77 K	22°C	450°C
H_2O on H_2O	0.5 eV/molecule	10^{15} s	10^{-5} s	10^{-9} s
H_2O on metal	1		10^{5}	10^{-5}
H_2 on Mo	1.7		10^{17}	1

Contact time for gas molecule impingng on a surface is about 10^{-12} seconds

3.3.2 Chemical Interactions

Atoms/molecules that condense on the surface can be:

- *Physisorbed,* i.e., form a weak chemical bond to the surface—this involves a fraction of an eV per atom binding energy (e.g. argon on a metal at low temperature).

- *Chemisorbed,* i.e., form a strong chemical bond to the surface (chemisorption)—this involves a few eV per atom binding energy (e.g., oxygen on titanium).
- *Diffuse* into the surface, i.e., absorption—often with dissociation (e.g. OH^- in glass, H^+ in metals, H_2O in polymers).
- *Chemically react* with the surface, i.e., diffuse and react in the near-surface region to form a compound layer (chemical surface modification).

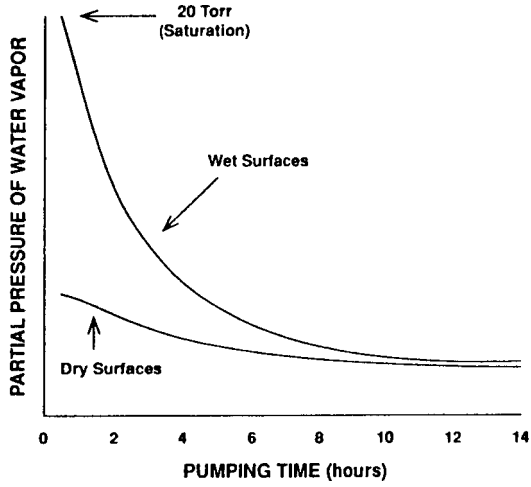


Figure 3-6. Typical pumpdown curve(s) for the removal of water vapor from a vacuum chamber: (*a*) starting with dry surfaces, (*b*) starting with wet surfces.

Table 3-6 lists some approximate values for the binding energy of atoms/molecules to clean surfaces. The binding energy of successive layers becomes the self-binding energy after several monolayers (ML) thickness. The amount of material adsorbed on a surface is dependent on the surface area. The "true surface area" can be determined by adsorption techniques and can be 10 to 1000 times the geometrical surface area on engineering materials and much higher on special adsorbent materials. True adsorption is a reversible process and the adsorbed materials can be driven from the surface by heating i.e., desorption. The adsorption process releases a heat of condensation. Absorption releases a "heat of solution." Chemical reaction can involve the release of heat (exothermic reaction) or may take up energy (endothermic reaction).

Table 3-6. Sorption Energies of Atoms and Molecules on Surfaces

Chemisorption (eV/atom or molecule)		Physisorption (eV/atom)	
Ni on Mo	2	Ar on W	0.1
H_2 on W	2	Ar on C	0.1
CO_2 on W	5		
O_2 on Fe	5.5		
O_2 on W	8.5		
H_2O on Metal	1.0		
H_2O on H_2O	0.5		

Absorption of a gas into the bulk of the material involves adsorption, possible dissociation, then diffusion into the material. The process of injecting gas into a surface is called "charging." Diffusion of gases, particularly hydrogen, into metals can be enhanced by exposure to a plasma and low energy ion bombardment.[26][27] Reasons for the rapid absorption of hydrogen from a plasma include:

- There is no need for molecular dissociation at the surface
- Surface cleaning by the plasma
- Implantation of accelerated ions into the surface producing a high chemical concentration thus increasing the "chemical potential" which is the driving force for diffusion

3.4 VACUUM ENVIRONMENT

A vacuum can be defined as a volume that contains fewer gaseous molecules than the ambient environment when both contain the same gaseous species and are at the same temperature. Even though the presence of "vacuum" was recognized and demonstrated in the 1600's[28][29] it was not until the 1900's that the vacuum environment was used for commercial thin film deposition.[30]

3.4.1 Origin of Gases and Vapors

Gases and vapors in the processing chamber can originate from:

- Residual atmospheric gases and vapors
- Desorption from surfaces, e.g., water vapor
- Outgassing from materials, e.g., water vapor from polymers, hydrogen from metals
- Vaporization of construction or contaminant materials
- Leakage from real and virtual leaks
- Permeation through materials such as rubber "O" rings
- Desorption, outgassing, and vaporization from introduced fixtures, tooling, substrates and deposition source materials ("brought-in" contamination)

These sources of gases and vapors determine the lowest pressure (base pressure) that can be reached in a given time (pumpdown time), the gas/vapor (contaminant) species in the system at any time, and how fast the chamber pressure rises after the pumping is stopped, i.e. the "leak-up rate" or "leak-back rate."

Several of these gas/vapor sources can become more important during processing due to heating and plasma desorption. For example, water adsorbed on surfaces is rapidly desorbed when the surface is in contact with a plasma. The effects of processing conditions on the vacuum environment are often very important and must not be neglected.

Water vapor from outgassing and desorption, is often the most significant contaminant species in typical film deposition vacuums in the 10^{-5} to 10^{-7} Torr range, while hydrogen from outgassing of metals is the most common species under ultrahigh vacuum conditions. The amounts of both these contaminants depend on the material, surface area and condition of the vacuum surface.

Residual Gases and Vapors

Residual gases and vapors are present from atmospheric gases and vapors that have not been removed. Table 3-7 shows the volume percentages, weight percentages and partial pressures of the constituents of air. The water vapor content is often the most variable and this variation is often the source of process variations.

Table 3-7. Composition of Air

Material		% by wt.	% by vol.	Partial Pressure (Pa)
		No water vapor		
N_2	28 amu	75.51	78.1	7.9×10^4
O_2	32	23.01	20.93	2.12×10^4
Ar	40	1.29	0.93	9×10^2
CO_2	44	0.04	0.03	31
Ne	20	1.2×10^{-3}	1.8×10^{-3}	1.9
He	4	7×10^{-5}	7×10^{-5}	0.53
CH_4	16	2×10^{-4}	2×10^{-4}	0.2
Kr	83	3×10^{-4}	1.1×10^{-4}	0.11
N_2O	44	6×10^{-5}	5×10^{-5}	0.05
H_2	2	5×10^{-6}	5×10^{-5}	0.05
Xe	131	4×10^{-5}	8.7×10^{-6}	0.009
O_3	48	9×10^{-6}	7×10^{-6}	0.007
		Water vapor at 50% RH, 20°C		
	18	1.6	1.14	0.115
Hydrocarbon vapors				Organic particulates
Non-hydrocarbon vapors				Inorganic particulates

Desorption

Desorption of adsorbed gases and vapors from a surface occurs by thermal activation, electron bombardment, photon bombardment, low energy ion bombardment ("ion scrubbing"), or physical sputtering. Increasing the temperature of the surface increases the desorption rate. Desorption rates (Torr-liters/sec-cm2) are very sensitive to the surface condition, coverage and surface area. For example, electropolished stainless steel surfaces have a desorption rate $^1/_{1000}$ of that of a bead-blasted surface, and aluminum with a chemically formed passive oxide layer, has a significantly lower desorption rate than one that has a natural oxide. The rate of desorption of water vapor from a stainless steel surface has been modeled assuming a porous oxide.[31] Thermal desorption can be used to

study the chemical binding of species to a surface.[32][33] In UHV technology a vacuum bake at 300–400°C for many hours is used to desorb adsorbed water vapor from surfaces.[34]

The water molecule is very polar and will strongly adsorb on clean metal and oxide surfaces. The amount of water vapor adsorbed on surfaces is dependent on the surface area and the presence of porosity which retains water in the pores. The amount of water vapor in the ambient air varies and can lead to variations in system performance and process reproducibility. It is generally a good practice to backfill a vacuum system with warm dry air or dry nitrogen. The flow of dry gas can continue through the chamber while the system is open, to minimize in-flow of air from the processing area. This backfilling procedure, along with heating the chamber walls while the system is open, and minimizing the time the system is open to the ambient, minimizes the water vapor adsorption on the interior surfaces of the vacuum system. Water vapor desorption can also be enhanced by backfilling (flushing) with hot-dry gas during the pumping cycle.

Outgassing

Outgassing, which is the diffusion of a gas to the surface where it desorbs, is typically a major source of gaseous contamination in a vacuum system.[31][35]-[37] Dense materials outgas by bulk diffusion to the surface followed by desorption. Porous materials outgas by surface or volume migration through the pores and along the pore surfaces to the surface where they desorb. Outgassing rates are expressed in units of Torr-liters/sec-cm^2 for gases or sometimes grams/sec-cm^2 for vapors such as water. Outgassing rates and amounts can be measured by weight-loss of the material as a function of temperature. Figure 3-7 shows some weight-loss rates for various polymer materials. When the material does not reach an equilibrium weight, then the matrix material is probably decomposing as well as desorbing water and other volatile materials. The outgassing is very dependent on the history of the surface and bulk material. For example, a polymer that has been stored outside in the rain will contain more water than one stored in a desiccated environment. Typically the outgassing rate doubles with every 5°C increase in temperature.

Organics and polymers outgas plasticizers, absorbed gases, water and solvents. Many polymers have absorbed several weight percent water and should be vacuum baked before use in a high vacuum system or where

water vapor is detrimental to the process or product. The time necessary to outgas a material depends on the materials to be outgassed, its thickness and the temperature. The necessary time/temperature parameters can be determined by weight-loss measurements or by mass spectrometer analysis of the vacuum environment during outgassing. Generally the highest temperature, consistent with not degrading the material, should be used in vacuum baking. A material can be said to be "outgassed" when it has less than 1% weight loss after being held at 25°C above the expected operating temperature for 24 hours at 5 x 10^{-5} Torr (*ASTM E595-90*).

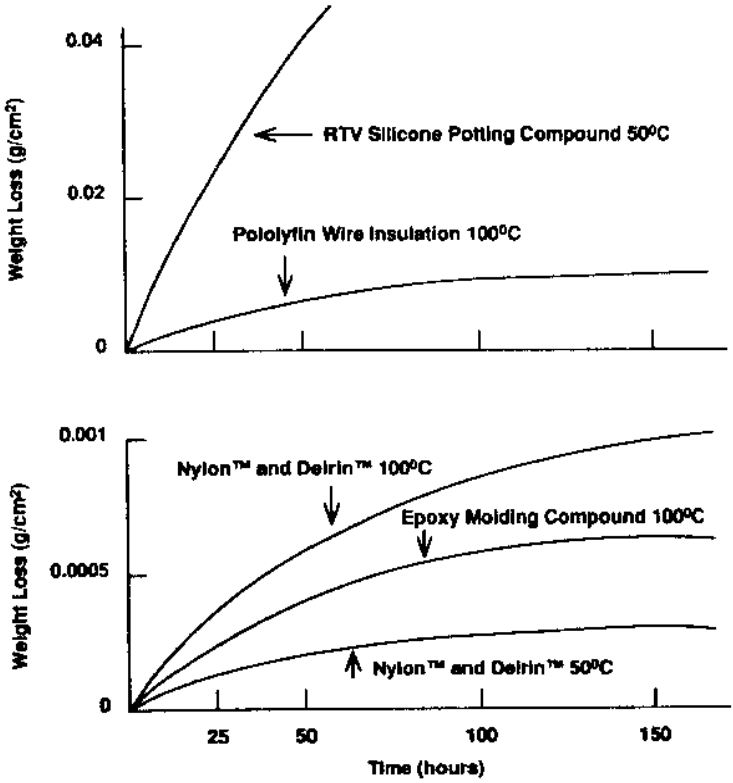


Figure 3-7. Weight loss as a function of time and temperature of several polymers in vacuum.

In some processing, apparent outgassing can result from the processing. For example, the evaporation of aluminum in a system containing water vapor can produce an apparently high hydrogen "outgassing"

because the aluminum reacts with adsorbed water vapor to release hydrogen. Another example is the high temperature (1000°C) hydrogen reduction of chromium oxide on stainless steel to form water vapor.[38]

Hydrogen is the principal gas released by dense metals.[39][40] The surface preparation of stainless steel, commonly used in the construction of vacuum vessels, determines the surface composition/chemistry, desorption and outgassing properties of the material.[41] Aluminum is also used in the vacuum environment and the outgassing properties of this material has been studied.[42]-[44] Glasses outgas water and other gases at high temperatures.

Outgassing of hydrogen from 300-series stainless steel may be decreased by high temperature vacuum firing of the material at 1000°C before installation in the vacuum system. Outgassing can be minimized by coating the stainless steel with gold, aluminum, or titanium nitride, which have low hydrogen permeability. Alternatively there are specialty stainless steels such as aluminum modified steels[45] which have low hydrogen outgassing properties.

Generally outgassing from dense metals, glasses, and ceramics is not important in PVD processing unless a very low contaminant level is necessary or very high temperatures are present in the chamber. However, outgassing from porous materials and polymers can be a substantial problem not only because it exists but because it is probably an uncontrolled process variable.

Outdiffusion

Outdiffusion is when the material that diffuses from the bulk does not vaporize but remains on the surface. For example, polymers often outdiffuse plasticizers from the bulk. These surface species then have a vapor pressure that contributes to the gaseous species. These outdiffused materials must be removed using surface cleaning techniques (Ch. 12).

Permeation Through Materials

Permeation (atomic or molecular) through a material is a combination of the solubility, diffusivity, and desorption of the gas or vapor particularly at high temperatures. Gases permeate many materials that are used in the construction of vacuum systems and components such as:

metals,[39][45] glasses,[46][47] ceramics, and polymers.[39][48] At low temperatures, the permeation of gases through polymers is the main concern, with permeation differing widely with the gas species. For example, oxygen, and water vapor permeate through Viton™ "O" rings much more rapidly than does nitrogen, carbon dioxide, or argon.[49] Permeation is not a concern with most PVD processing.

Vaporization of Materials

Atoms or molecules of a material may vaporize from the surface of a liquid or solid of that material. The equilibrium vapor pressure of gaseous species above a liquid or solid in a closed chamber is the pressure at which an equal number of atoms are leaving a flat surface as are returning to the surface at a given temperature. The equilibrium vapor pressure of a material is strongly dependent on the temperature, and the vapor pressures of different materials at a given temperature may be vastly different. Raoult's Law states that constituents from a liquid vaporize in a ratio that is proportional to their vapor pressures.

The lowest pressure that can be achieved in a vacuum system is determined by the vapor pressure of the materials in the system. For example, in a system containing a flat surface of liquid water at room temperature (22°C) the lowest pressure that can be obtained is about 20 Torr, until all the water has been vaporized. In pumping water vapor from a system the vapor from the surface of a thick layer of water will leave quickly, the water near the solid surface will leave more slowly and finally the water from capillaries will leave even more slowly. Figure 3-6 shows a typical pumpdown curve for water vapor in a vacuum system. Note that there is still appreciable water vapor even after hours of pumping.

Table 3-4 shows the equilibrium vapor pressure of water. If the temperature of a surface is below -100°C then water frozen on the surface has a very low vapor pressure. This is the principle of the cryocondensation trap where large area cold surfaces are used in the deposition chamber to "freeze-out" contaminant vapors such as water vapor.

When the atoms/molecules that leave the surface do not return to the surface the process is called "free surface vaporization." Evaporation results in evaporative cooling of the surface since the heat of vaporization is taken away from the surface by the evolved species. Rapid evaporation of water can result in freezing of the water in a vacuum system and this ice sublimes slowly.

Real and Virtual Leaks

Real leaks connect the vacuum volume to the outside ambient through a low-conductance path. Real leaks may be due to:

- Porosity through the chamber wall material*
- Poor seals
- Cracks
- Leaks in water cooling lines within the vacuum system

Real leaks are minimized by proper vacuum engineering, fabrication and assembly.

Virtual leaks are internal volumes with small conductances to the main vacuum volume. Virtual leaks may be due to:

- Surfaces in intimate contact
- Trapped volumes, e.g. unvented bolts in blind bolt holes or pores in weld joints

A common area for a virtual leak is the mechanical mounting of a part on a surface. The virtual leak is from the entrapped volume between the part and the surface. Virtual leaks are minimized by proper design and construction. The evacuation of virtual leaks is aided by heating. The determination of whether a leak is real or virtual can take appreciable detective work. One technique is to backfill with an uncommon gas such as neon. On pumpdown, if the neon peak in a mass spectrometer spectrum disappears rapidly the leak is probably a real leak, but if it decreases slowly it is probably a virtual leak.

The presence of leaks in a system can be detected by several means including:[50][51]

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*Porosity in metals. Knowing the problem of porosity in melted steels, vacuum melted electronic grade Kovar™ was ordered to avoid the potential porosity problem. The parts were machined out of $^{1}/_{2}$" bar stock with a wall thickness of $^{3}/_{8}$". On one batch of material, the components leaked, and it was thought that a sealing problem existed. Porosity in the Kovar™ housing was not suspected. It turned out that one Kovar™ rod had porosity even though it had been vacuum melted. To avoid the problem, a vacuum leak test of the housing after machining but before sealing was instituted.

- A behavior different from previous condition, i.e. baseline condition of the system when it is working well. The baseline condition should include:
  - time to reach a specified pressure
  - leak-up rate through a given pressure range
- Detection of an indicator gas—usually helium
- Change in behavior when the ambient is changed—large molecules may plug small leaks and allow a lower base pressure

The leak rate is the amount of gas passing through a leak in a period of time and depends on the pressure differential as well as the size and geometry of the leak path. Leak rates are given in units of pressure-volume/time such as Torr-liters/sec. Real leaks can be determined by using a calibrated helium leak detector.[52]-[54] Helium should be applied to local areas and used from the top down since helium is lighter than air. The speed of movement of the helium probe is important since small leaks can be missed by a fast-moving probe. A coaxial helium jet surrounded by a vacuum tube has been used with success to isolate leak locations.[55] Leak rates down to 10^{-9} Torr-liters/sec of nitrogen can be detected using helium leak detection methods. For accurate measurement the leak detector must be calibrated with a standard leak.

Determining the location of a leak after assembly may be difficult—particularly if there are a large number of leaks. To minimize leaks in the assembled system, all joints and subsystem components should be helium leak checked during assembly. An efficient way of finding leaks is to leak check the subassemblies, assemble and leak check the simple system, and then add other subassemblies. As a final leak check, the system can be covered with a plastic bag and the bag filled with helium (bag check) to determine the cumulative effect of all leaks. As a baseline for system behavior a new system should be "bag-checked" to determine its total leak rate. A good production system might have a total leak rate of 10^{-5} Torr-liters/sec as-fabricated.

"Brought-in" Contamination

Gases and vapors can originate from desorption, outgassing, and vaporization from introduced fixtures, tooling, substrates and deposition source materials. This is called "brought-in" contamination. This type of

contamination is minimized by proper cleaning and handling of surfaces before being placed in the system (Ch. 12).*

3.5 VACUUM PROCESSING SYSTEMS

A generalized layout for a vacuum processing system, is shown in Fig. 3-8. The deposition chamber is comprised of removable surfaces, such as fixturing and substrates, and non-removable surfaces.

The vacuum processing system consists of:

- A processing chamber—optimized for production, or flexible for development.
- Chamber fixturing, tooling and associated feedthroughs, and other components—optimized for production or flexible for development; designed for accessibility and maintenance.
- Vacuum pumps with associated plumbing (pumping stack)—designed for required cycle-time, maintenance, fail-safe operation, etc.
- An exhaust system—designed with environmental and safety concerns in mind.
- A gas manifolding system—for the introduction of processing gases (if used) and backfilling gas.

At present there is no universally accepted set of symbols for the various vacuum components although various groups are working on the problem. In manufacturing, every deposition system should have a schematic diagram of the system to enable the system to be explained to operators and engineers. This should be posted on the system.

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*A process had completely deteriorated in a contaminate-sensitive deposition process. The technician decided that the system had become contaminated by backstreaming from the vacuum pump. The fixturing was moved to another system without being cleaned where it contaminated that system. Two systems "bit-the-dust" for one mistake. The cleaning and conditioning of the fixturing before being placed in the deposition system is just as important as cleaning the substrates.

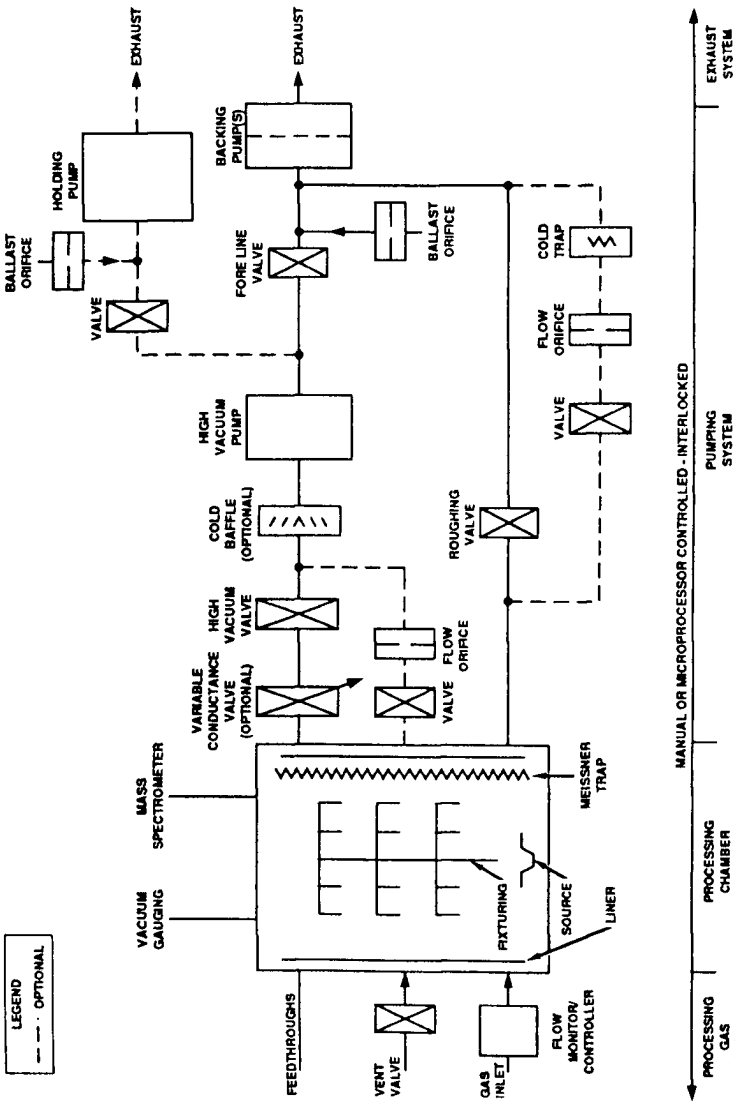


Figure 3-8. Vacuum/plasma processing system.

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3.5.1 System Design Considerations and "Trade-Offs"

Each PVD processing application has unique challenges that influence the design and operation of the deposition system.[56] These factors should be carefully considered. Some general concerns are:

- Access—how large and heavy are the parts and fixturing?
- Do the parts need to have *in-situ* processing? e.g. outgassing, heating, plasma treatments, etc.
- System cleaning—is there a lot of debris generated in the process? Does the debris fall into critical areas such as valve sealing surfaces? How often will system cleaning be necessary?
- Cycle time for the system—production rate.
- How often do fixtures and tooling need to be changed?
- Is the processing sensitive to the processing environment?
- Sophistication of the operators—operator training.
- Maintenance.
- Safety aspects—high voltage, interlocks.
- Fail safe design—short or long power outages, water failure.
- Environmental concerns—exhaust to the atmosphere, traps.

When a system is optimized for production, the internal volume and surface area should be minimized commensurate with good vacuum pumping capability. However, if appreciable water vapor is being released in the chamber or if reactive gases are being used for reactive deposition, "crowding" in the chamber can interfere with pumping of the water vapor or the gas flow, creating problems with "position equivalency" for the substrate positions during deposition. This can lead to a variation in product as a function of position in the deposition chamber.

The non-removable surface should be protected from film-buildup, corrosion, and abrasion. This may necessitate the use of liners and shields in the system to protect the surface from the processing environment or minimize the need for cleaning of the non-removable surfaces.

3.5.2 Processing Chamber Configurations

Figure 3-9 shows some deposition chamber configurations.

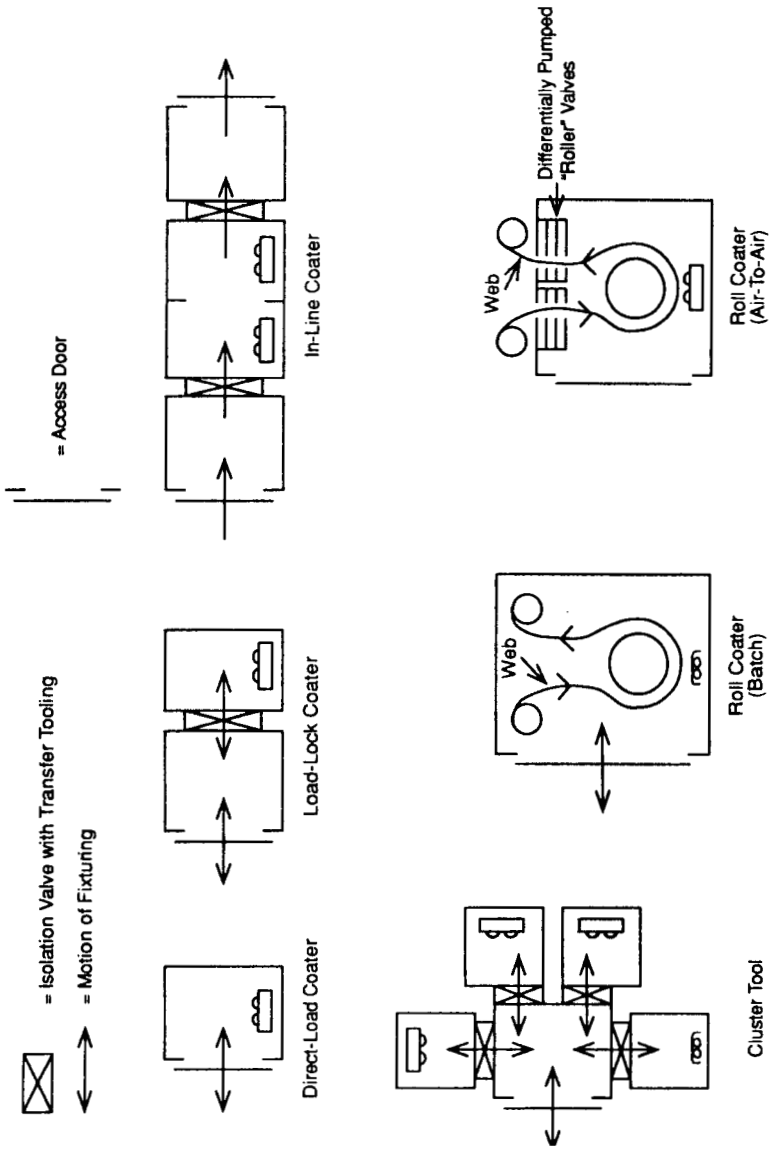


Figure 3-9. Deposition chamber configurations.

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Direct-Load System

In a direct-load or batch-type system (no load-lock) the processing chamber is opened to the ambient for loading or removing the parts to be processed and/or introducing the materials used in processing. An advantage of this type of system is that it is the least expensive and the most flexible of the chamber configurations. A problem with this chamber configuration is the contamination of surfaces that occurs when the system is open that can lead to undesirable process variability. In many cases, process variability can be traced to changes in the relative humidity and/or the time that the system is opened to the ambient.*

Figure 3-10 shows a direct-load system with a large door for easy access which was designed for post-cathode magnetron sputter deposition of films on the inside diameter of a large ceramic cylinder.[57] Figure 3-11 shows a schematic of the system. The system uses a mechanical pump and sequenced sorption pumps for roughing the chamber and a cryopump for high vacuum pumping the chamber. Pressure is monitored and controlled by a capacitance manometer gauge and servo-controlled leak valve.

In some cases the processing chamber is bulkhead mounted so that it is in a separate room from the pumping system. This means that vacuum pump maintenance and associated potential for contamination are isolated from the processing environment. This is particularly useful in cleanroom applications when oil-containing vacuum pumps are used and where noise abatement is desirable.

Load-Lock System

In the load-lock system the processing chamber remains isolated from the ambient. In operation, the parts are placed into an outer chamber where they may be outgassed and heated. The outer chamber is pumped down to the processing chamber pressure, the isolation valve opened, and

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*There was trouble with reproducibility on the production line. An investigation found that a batch-type vacuum system was being used with a belljar lift and a swing-out motion. The problem was that after swinging, the belljar was positioned over the cold exhaust of the liquid nitrogen trap. On a humid day, water was actually condensing on the interior of the belljar.

the parts transferred to the processing chamber. After processing, the parts are removed back through the outer chamber. Since the processing chamber is not opened, a long-lived vaporization source, such as a sputtering cathode or replenishing system such as a wire-fed evaporation source, is required.

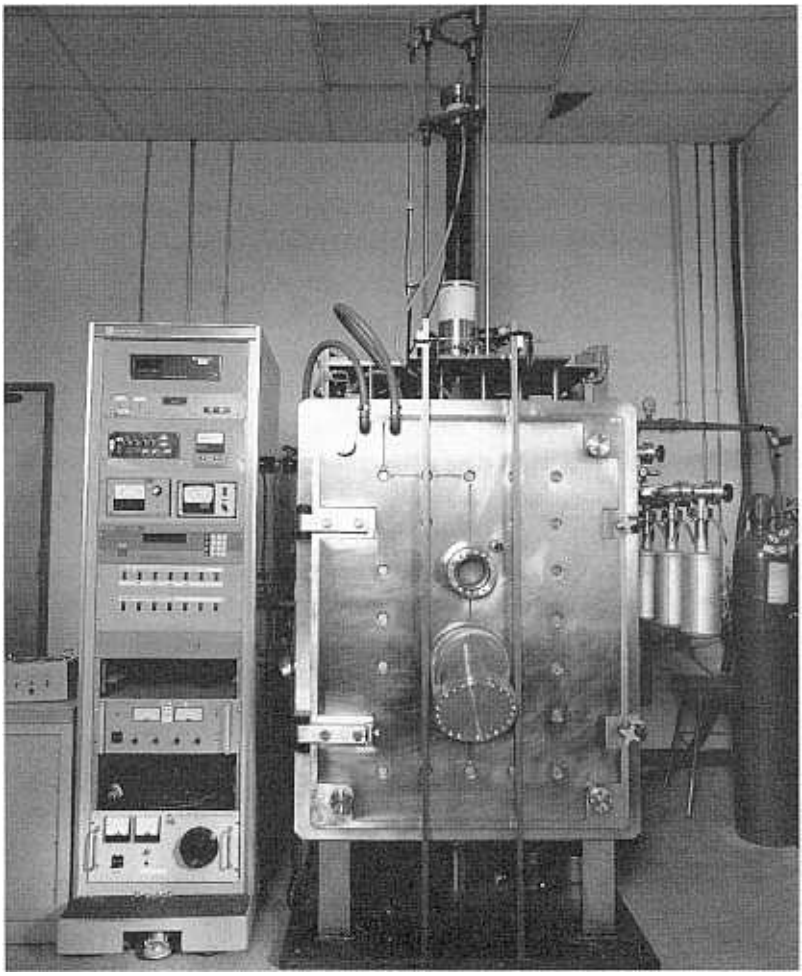


Figure 3-10. Picture of the BOLVAPS vacuum deposition system.

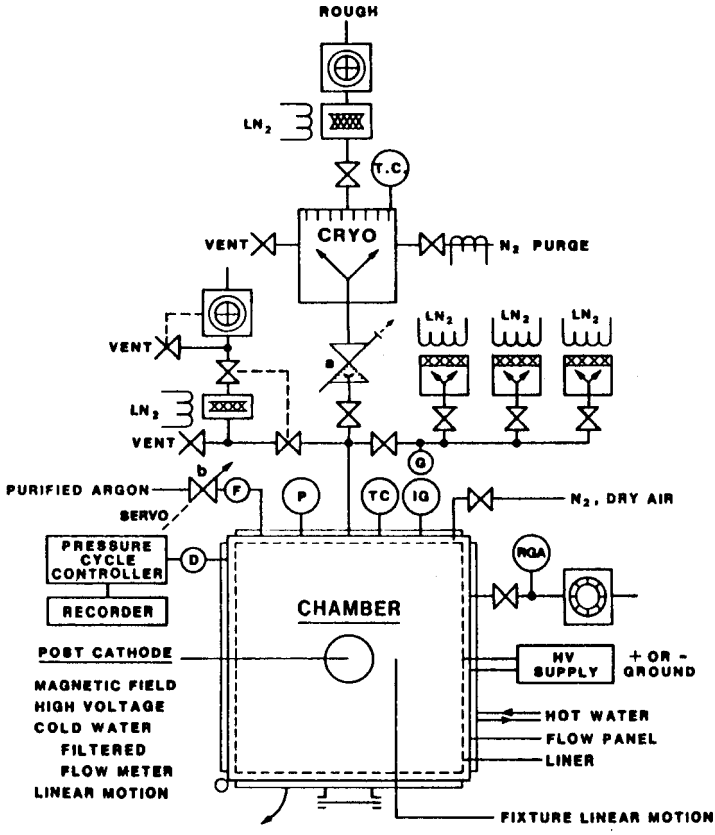


Figure 3-11. Schematic of the BOLVAPS vacuum deposition system.[57]

In-Line System

In an in-line system several lock-load processing modules are in series so that the substrate passes sequentially from one to the next and out through an exiting chamber. Since the processing chamber is not opened, a long-lived vaporization source such as a sputtering cathode or a replenishing system such as a wire-fed evaporation source is required. The lock-load system configuration is suitable for automation and production at rather high volumes. The lock-load system can be used with very large rigid structures such as architectural glass.

Cluster Tool System

The cluster tool system uses a central introduction chamber from which the substrates may be moved into separate processing modules through load-locks and transfer tooling. These processing modules may include operations such as plasma etching, which is a very dirty process, as well as deposition processes such as sputter deposition or CVD. The modules may be arranged so that there is random access to the various modules.

The cluster system, along with using a nitrogen blanket and isolation technology, is an important part of the "closed manufacturing system" for silicon device manufacturing where a silicon wafer is not exposed to the cleanroom ambient at anytime during manufacturing.[58]

A design criteria for a modular system is to have standard flanging to allow joining the modules from different manufacturers. This type of interfacing is sometimes referred to as SMIF (Standard Mechanical Interfacing).[59][60] Standards for such interfacing are being developed by the SEMI Modular Equipment Standards Committee.

Web Coater (Roll Coater)

The roll coater or web coater is a special batch-type system that allows coating of a flexible material ("web") in the form of a roll.[61][62] This type of system is used to coat polymer and paper material which is then sent to the "convertor" to be processed into the final product. The system fixtures and tooling un-rolls the material, passes it over a deposition source and re-rolls the material at a very high rate. For example, a web coater is used to deposit aluminum on a 100,000 foot long by 120 inch wide, 2 mil plastic material moving at 2000 feet/min. Web thicknesses typically range from less than 48 gauge (12 microns or $^1/_2$ mil) to 700 gauge (175 microns or 7 mils) of materials such as polyethylene terephtalate (PET). Coating may be on one or both sides and the deposition process is usually vacuum deposition. However, reactive sputter deposition, plasma polymerization, and plasma enhanced CVD are used for some applications.

Air-To-Air Strip Coater

In an air-to-air strip coater, a continuous strip of material passes into and out of the deposition chamber through several differentially-pumped slit or roller valves. This type of system has been used for coating strip steel with zinc and aluminum and for coating flexible polymers.[63][64]

3.5.3 Conductance

The conductance of a portion of a system is a measure of its ability to pass gases and vapors and is defined by the pressure drop across that portion of the system. A design that restricts the free motion of the molecules decreases the conductance of the system. Such restrictions can be:

- Fixturing in the chamber
- Small diameter plumbing
- Baffles
- Long runs of plumbing
- Valves
- Bends in tubing
- Traps
- Screens

In molecular flow, the conductance of a tube is proportional to the ratio of the length-to-radius (L/r). Table 3-8 shows the relative flow rates of gases through an orifice and through various tubes with a length, L, and a radius, r.

Table 3-8. Relative Flow Through Tubes and an Orifice

Tube length	L/r	Flow relative to an orifice
Orifice	0	100%
L = r	1	75
L = 2r	2	60
L = 4r	4	40
L = 8r	8	25

The conductance of plumbing in a vacuum system is analogous to the electrical resistance of an electrical system. The conductance, C, of a flow system in series (series flow) is given by:

Eq. (3) $C_{total} = C_1 + C_2 + C_3 + \ldots$

where C_1, C_2, C_3 … are the conductances of each portion of the system.

The conductance of a flow system in parallel (parallel flow) is given by:

Eq. (4) $1/C_{total} = 1/C_1 + 1/C_2 + 1/C_3 + \ldots$

The conductance of the system can be the limiting factor in the pump speed since the pumping speed can be no higher than that allowed by the conductance of the system and the effect of conductance losses can be dramatic.* For example, the effective pumping speed of a 2000 l/sec pump attached to a chamber by a 4" diameter pipe 20" long will be 210 l/sec. If the pump size is increased to 20,000 l/sec the effective pumping speed will only be increased to 230 l/sec. The conductance of the exhaust system is also important since a restricted conductance can create a back pressure on the vacuum pump especially during startup.

Conductance assumes no adsorption-desorption mechanism for the gaseous/vapor species. Since vapors have an appreciable residence time on surfaces and gases do not, the conductance for vapors is often significantly lower than the conductance for gases since the vapors must be adsorbed and desorbed from the surfaces as they make their way through the system.

In processing, it is often desirable to have a high initial pumping speed to allow a rapid cycle time, but to have a low pumping speed during the process to limit the flow of processing gases. This may be accomplished

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*A deposition system was being pumped through a port in the baseplate (base-pumped). During filament evaporation of aluminum, occasionally some of the aluminum would fall off and drop into the pumping stack or on the valve sealing surface. To prevent the problem, the operator placed a piece of screen wire over the pumping port. This solved the problem but cut the pumping speed about in half. The problem should have been solved by placing a container below the filament to catch any drips or in the design stage by having a side-pumped deposition system.

by limiting the conductance. Ways of limiting the conductance of a pumping manifold in a controllable manner include:

- Throttling (partially closing) the main high vacuum valve
- Use a variable conductance valve in series with the high vacuum valve as shown in Fig. 3-8
- Use an insertable orifice in series with the high vacuum valve
- Bypass the high vacuum valve with a low conductance path, e.g. the optional path shown in Fig. 3-8

A problem with limiting the conductance is that the ability to remove contaminants is also reduced. Since water vapor is the prime contaminant in many systems, this problem can be alleviated by having a large-area cryocondensation trap (cryopanel) in the chamber to condense the water vapor. This trap should be shielded fom process heat.

In systems having greater than a few microns gas pressure, particularly those having a significant amount of fixturing, there may be pressure differentials established in the processing chamber with the lower pressure being nearest the pumping port. This pressure differential may affect pressure-dependent processes parameters and film properties such as residual stress and chemical composition in deposited thin films.

3.5.4 Pumping Speed and Mass Throughput

In a vacuum pump, the pumping speed for a specific gas at a given pressure and pressure differential (i.e. chamber pressure and pressure on exhaust side) can be expressed in units of volume per unit time as:

$$1 \text{ liter/sec} = 2.12 \text{ ft}^3\text{/min (CFM)} = 3.6 \text{ m}^3\text{/hr (CMH)}$$

Each pump has a specific pumping speed curve showing the pumping characteristic of the pump as a function of inlet pressure, exhaust pressure, and gas species. Pumping speeds are generally measured and rated either in accordance with the *American Vacuum Society Recommended Practices* or the *International Standards Organization (ISO) Standards.* The gas throughput (Torr-liters/sec) can be calculated from the pump speed and the pressure.

Many factors affect the performance of a vacuum pump and that in turn affects the pumping speed. Pumping speeds are normally rated over a specific pressure range. Diffusion and turbomolecular pumps provide relatively flat pumping speed curves throughout the molecular flow range to near their ultimate vacuum. Ion pumps and cryopumps are rated for peak pumping speeds at certain pressures for certain gases. Different pumping techniques have different efficiencies for pumping different gases. For example, cryopumps and ion pumps do not pump helium well and turbopumps do not pump water vapor well.

The "real pumping speed" is defined as the pumping speed at the processing chamber, i.e. after the conductance losses. For a pump with a speed, S_p, connected to a chamber with a pipe of conductance, C, the "real pumping speed", S_{real}, is given by:

Eq. (5) $S_{real} = S_p C / (S_p + C)$

A high pumping speed at the chamber, may or may not be necessary in a vacuum processing system. For example, for rapid pumpdown a high conductance is desirable and the plumbing should be so designed. However, if outgassing is a concern, the pumpdown time to a given "leakup rate" is not pump-limited but is outgassing-limited and the required pumping speed may be smaller.

The throughput (Q) of a portion of a vacuum system is the quantity of gas that passes a point in a given time (Torr-liters/sec).

Eq. (6) $Q = S$ (pumping speed) x P (gas pressure at that point)

3.5.5 Fixturing and Tooling

There is no general definition of PVD fixtures and tooling but fixtures can be defined as the removable and reusable structures that hold the substrates, and tooling can be defined as the structure that holds and moves the fixtures and generally remains in the system. Fixtures are very important components of the PVD system. The number of substrates that the fixture will hold and the cycle-time of the deposition system determine the product throughput or number of substrates that can be processed each hour. For example, compact (music) discs (CDs) were initially coated in batches of several hundred in a large batch-type deposition chamber. Now they are coated one-at-a-time in a small deposition chamber, which is

integrated into the plastic molding machine, with a cycle time of 2.8 seconds. To achieve the same throughput in a large batch-system holding 500 CDs would require a cycle time of about 25 minutes and would be difficult to integrate into the plastic molding operation.

The fixtures may be stationary during the deposition but often they are moved so as to randomize the position of the substrates in the system during deposition so that all substrates see the same deposition conditions. This will insure that all the deposited films have the same properties (i.e., position equivalency). Often the fixtures have a very open structure. Figure 3-12 shows several common fixture configurations. Figure 3-12a depicts a pallet fixture on which the substrate lies and is passed over the deposition source. The planar magnetron sputter deposition source provides a dual-track linear vaporization pattern of any desired length. By making the linear source longer than the substrate is wide, a uniform film can be deposited. This type of fixture is used to deposit films on 4 inch diameter silicon wafers and 10 foot wide architectural glass panels. This type of fixture has the advantage that the substrates are held in place by gravity.

Figure 3-12b shows a multiple pallet fixture that can be used to deposit multilayer films on several substrates by passing them over several sources that are turned-on sequentially or to deposit alloy or mixture films by having the sources on all at once. Figure 3-12c shows a drum fixture where the substrates are mounted on the exterior or interior surface of the drum and rotated in front of the vaporization source(s) which are located on the interior or exterior of the drum. The drum can be mounted horizontally or vertically. Horizontal mounting is used when the vaporization source is a linear array of evaporation sources such as in the evaporation of aluminum for reflectors. Vertical mounting is often used when the vaporization source is a magnetron sputtering source. The drum fixture has the advantage that the substrates can be allowed to cool during part of the rotation so that temperature-sensitive substrates can be coated without a large temperature rise.

Figure 3-12d shows a 2-axis drum fixture that can be mounted horizontally or vertically. This type of fixture is used to coat 3-dimensional substrates such as metal drills, as shown in Figure 3-13, and complex-curvature surfaces such as auto headlight reflectors. By having an open structure, the fixture allows deposition on the part, even when it is not facing the vaporization source.

Figure 3-12e shows a hemispherical calotte fixture where the substrates are mounted on a rotating fixture which is mounted on a section of a hemisphere which is rotated. When using a vaporization source that is of small diameter, such as an evaporation filament that is mounted at the center of the sphere, all points on the sphere are equidistant from the source which aids in depositing a uniformly thick film. Uniform coatings on the interior surface of the calotte can be formed using an S-gun magnetron source(s) which has a broad vaporization plume. This type of fixture is often used to coat optical components.

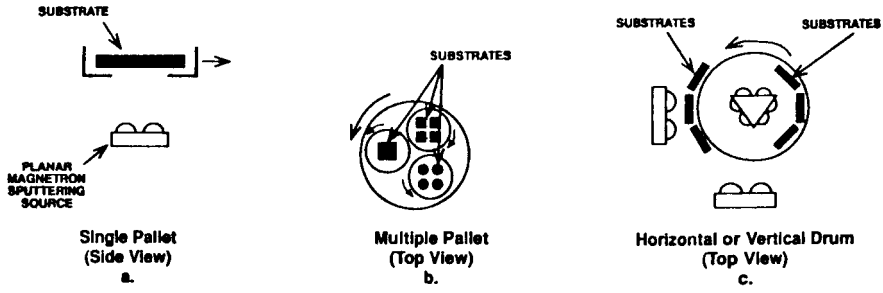


Figure 3-12*a, b, c*. Some common fixture configurations; (*a*) Single Pallet (side view); (*b*)Multiple Pallet (top view); (*c*) Horizontal or Verticle Drum (top view).

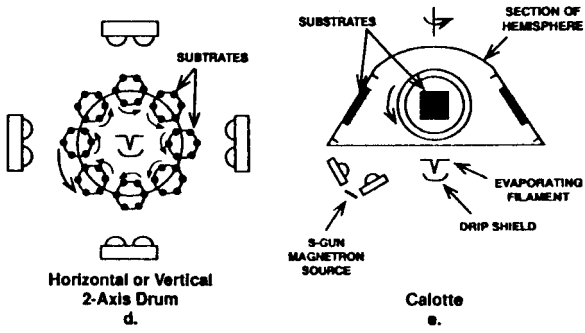


Figure 3-12*d* and *e*. (*d*) Horizontal or Vertical 2-Axis Drum; (*e*) Callote.

Figure 3-12f shows a barrel fixture which has a grid structure that contains the substrates.[65] By rotating the cage, the substrates are tumbled and all surfaces are exposed to the deposition. This type of fixture is use to coat small substrates such as aluminum-coating titanium fasteners for the aerospace industry.[66] To coat balls, such as ball-bearings, a shaker-table can be used.

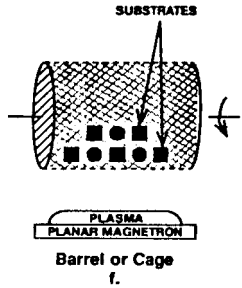


Figure 3-12*f*. (*f*) Barrel or cage.

When using fixtures where gravity cannot be used to hold the substrates on the fixture some type of mechanical clamping must be used. The clamping points will not be coated so the substrates and film structure should be designed with this in mind. If 100% coverage is necessary, a cage fixture can be used or the substrate can be moved during the deposition so as to change clamping points and allow full coverage. In some cases the substrate must be coated a second time.

Some fixture designs must be such that the fixtures can be passed from one tooling arrangement to another such as is used in load-lock systems. In some applications, such as in sputter cleaning or in ion plating, a high voltage must be applied to the fixture. If the fixture is rotating or translating, electrical contact for DC power must be made through a sliding contact. Often this is through the bearings used on the rotating shaft. Wear, galling, and seizure of the contacts can be minimized by using hard materials in contact, using an electrically conducting anti-seize lubricant such as a metal selenide, or by using non-sticking contacting materials such as osmium-to-gold. If high currents are used, the contacting areas should be large. For rf power to be applied to the fixture, the surfaces need not be in contact since the non-contacting surfaces can be capacitively coupled.[67]

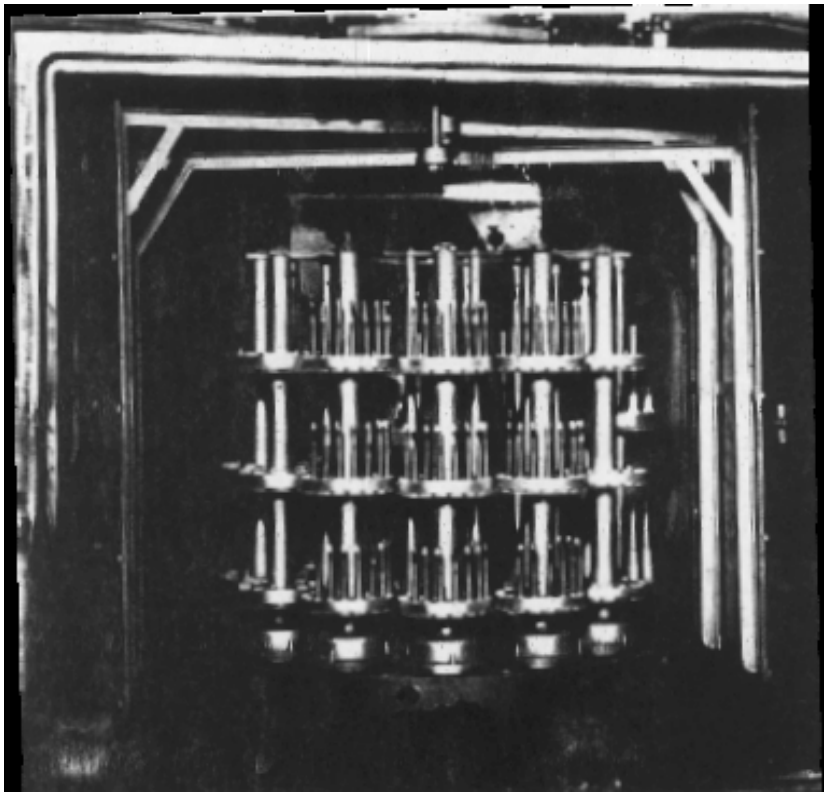


Figure 3-13. A 2-axis drum fixture for coating toolbits (Courtesy of Hauzen Techno Coatings).

Moving surfaces in contact can generate particulates in the deposition system. If these particles fall on substrate surfaces they will generate pinholes in the deposited film. Proper design of the fixturing will minimize this problem. In some cases, the fixturing is roughened by bead blasting to increase the adhesion of film-buildup to the surface. This decreases the flaking of the film buildup from the surface.

The deposition system should be designed around the fixture to be used. Often the fixture has a limited lifetime and represents a major capital investment and careful thought should be given to its design. The surface of the fixture can have a large surface area and it should be cleaned and handled carefully to prevent it from introducing contamination into the system. Often several fixtures are available so one can be used while the others are in the process of being stripped, cleaned, and loaded with substrates.

Tooling can also be used to move the vaporization source.[66] This is useful when coating a large part in a relatively small chamber. Tooling can also be used to move masks and shutters.[68]-[70]

Substrate Handling

Substrate handling includes unpacking, substrate preparation, racking in the fixture, loading the fixture, unloading, and packaging. When designing a high throughput production deposition system the handling rate is an important and possibly even limiting factor. When such a system is contemplated, the total system must be designed as a unit. Often in high throughput production, substrate handling must be done with robotics and the substrate handling cost may exceed the cost of the deposition system. For lower throughput systems substrate handling is usually done manually.

3.5.6 Feedthroughs and Accessories

Linear and rotational motion can be introduced into the chamber using mechanical or magnetic feedthroughs. Mechanical feedthroughs can use metal-bellows, which allow no leak path, differentially pumped O-ring seals, which should be lubricated, or ferrofluidic seals. Heating of moving fixtures can be done by radiant heating from quartz lamps, by electron bombardment, or, in the case of sputter cleaning and ion plating, by ion bombardment. Cooling of stationary fixtures can be done using liquids or gases such as helium which has a high thermal conductivity. Cooling of the moving fixtures is difficult but can best be done by having a cold, infrared absorbing surface near the fixture so radiant cooling is most effective. In some cases, rotating gas or liquid feedthroughs can be used to cool solid moving fixtures such as the drum fixture. These types of feedthroughs often present problems with use and should be avoided if possible.

3.5.7 Liners and Shields

Liners and shields are used to prevent deposition on non-removable vacuum surfaces. The liners and shields can be disposable or they may be cleaned and reused. Aluminum foil is a common disposable liner material. The common aluminum foil found in grocery stores is coated

with oil and should be cleaned before being placed in the vacuum system. Clean aluminum foil can be obtained from semiconductor processing supply houses.

3.5.8 Gas Manifolding

Vapors and particulates can be brought into a system through the gas distribution lines when gases are used. **Beware of gases from in-house gas lines!!!** Often they are contaminated by the way they were installed or during maintenance. Gases should be distributed through a non-contaminating manifold system. Generally such a system is made of stainless steel or a fluoropolymer such as Teflon™.

In some plasma applications "speciality gases", such as HCl, HBr and WF_6, which contain halogens, are used. These gases will corrode stainless steel if moisture is present. Moisture retention is a function of surface area. Electropolishing or slurry polishing, followed by an oxidation treatment is the best surface treatment for reducing the outgassing from the interior surfaces of stainless steel tubing.[71]-[73] For critical applications, the electropolished surface is analyzed for the chromium-to-iron ratio (typically 3:1), the chromium oxide-to-iron oxide ratio (typically 5:1), and the surface finish (typically an R_a of 2 microinches). The stainless surface can also be passivated using organosilanes which form a hydrophobic surface layer on the stainless steel.[74] The organosilanes also aid in removing water from the distribution lines by chemically reacting with the water.

Venting (backfilling) is the procedure for returning the vacuum chamber to the ambient pressure. This is best done using dry nitrogen or dry air (10 ppm H_2O). If this venting takes place rapidly, particles can be stirred-up in the system. To avoid this problem a "soft-vent" valve can be used to allow the pressure to rise slowly enough in the system so that turbulence is avoided.[23][24] Backfilling with a dry gas can generate a static charge on an insulator surface if the venting gas is directed toward the surface. This will cause particles to be attracted to the surface.

If reactive gases are used in the processing, gas injection into the deposition system should be such that the gas availability should be uniform over the surface of the depositing film. Usually it is best to not aim the gas flow directly at the substrates but to direct it in a manner such that there will be multiple collisions with surfaces before it reaches the film surface. This helps to provide uniform availability over the surface. Often

the gas is used to form a plasma and the availability should be uniform throughout the plasma generation region. Injection uniformity is usually accomplished by using a manifold with multiple orifices located in the region of interest. The distribution piping should be large to minimize pressure differentials along the length and the orifices may be of differing sizes to control the flow.

Mass Flow Meters and Controllers

Mass flow is measured in units of volume-pressure per unit time such as Torr-liters/sec, mbar-liters/sec or standard (760 Torr, 0°C) liters per minute (slm). At 0°C, 1 slm equals about 5 x 10^4 Torr-liters/sec and about 2.7 x 10^{21} molecules per minute.

The most common gas mass flow meters (MFM) use cooling by the flowing gas as the basis of measurement.[75][76] An element is heated by electrical power to about 100°C and the power needed to maintain a constant temperature, or the temperature at a constant power, or a temperature gradient is measured. The output from this measurement is used to indicate the gas flow by appropriate calibration. The output can be used to control the flow through a metering valve located either upstream or downstream from the mass flow meter to give a Mass Flow Controller (MFC) as shown in Fig. 3-14. The opening through the metering valve is generally controlled by an electromagnetic solenoid or piezoelectric actuator. The metering valve should never be used as a gas shut-off valve. Other types of flow meters are the rotating vane (rotameter) type and the gas-levitated ball meters.

The cooling rates by different gases varies. Therefore the calibration of the MFM varies with the gas species. For example, relative correction factors for one make of MFM is nitrogen = 1.0, argon = 1.45, helium = 1.45 and CH_4 = 0.72. The cooling rate also depends on the amount of turbulence in the gas flow so the flow meters are designed for specific mass flow ranges. The most reproducible measurements are made with a laminar gas flow so the gas flow is split in the meter to allow laminar gas flow to be established in the branch used for flow measurement. The MFC should be periodically calibrated when used in critical applications such as reactive deposition processing.[77][78] For PVD processing, mass flow meters are available to measure gas flow rates from about 0.1 sccm (standard cubic centimeters per minute) to over 100 slm (standard liters per minute) with inlet pressures from a few tens of psi down to 100 Torr.

The gas mass flow meters generally are designed to only withstand several hundred psi inlet pressure. Higher pressures can result in the violent failure of the meter. Since the gas source for PVD processing is often from high pressure gas cylinders it is important that the full cylinder pressure never be applied to the flow meter. This is accomplished by using a pressure regulator on the gas cylinder and including an appropriate flow restrictor and pressure relief valve in the gas line as shown in Fig. 3-14. In the event that the regulator fails, the flow restrictor causes the line pressure to increase to the point that the pressure relief valve is actuated before pressure in the downstream line exceeds the design pressure of the mass flow meter.

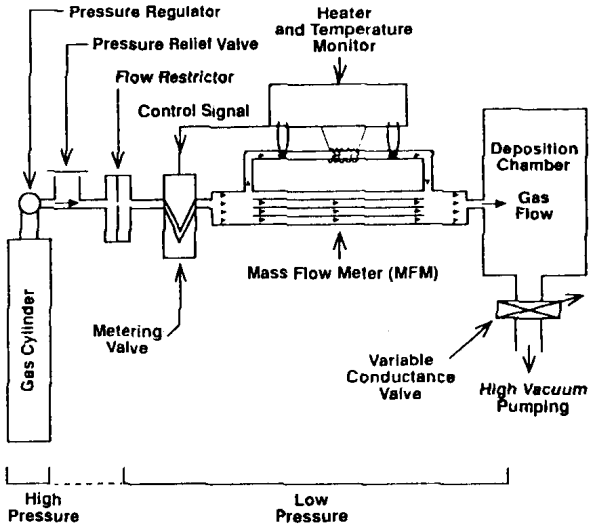


Figure 3-14. Mass flow controller and gas distribution system.

When using a flow of processing gas into the deposition chamber the high vacuum pumping speed is generally reduced to limit the gas flow through the system. This can be done by having a variable conductance valve (throttling valve) in the high vacuum pumping line as shown in the Fig. 3-8 or by using a bypass line containing a flow-control orifice in the pumping manifold. A typical flow rate for argon in a sputtering process is about 100 sccm (1.267 Torr-liters/sec).

Mass flow through the deposition chamber during processing using inert gases can be an important deposition parameter since it determines of how much "flushing-action" takes place in the chamber. This

flushing-action carries contaminate gases and vapors from the deposition chamber. In a low-flow or static system, the contaminate level can buildup during processing.

In reactive deposition processes, such as the deposition of titanium nitride (TiN) the mass flow is important in making the reactive gas (nitrogen) available during the deposition. It should be recognized that the reactive gas is pumped in the deposition chamber by reaction with the freshly deposited film material ("getter-pumped"). The means that the amount of reactive gas available for reaction in the chamber will depend on a number of factors other than the mass flow into the chamber. These factors include the deposition rate and the area on which the film is being deposited ("loading factor"). The way the reactive gas is introduced into the deposition chamber can also affect the reactive gas availability so the gas injection geometry is an important design consideration in reactive deposition processing, particularly if the reactive gas flow rate is low. Special mass flow meters and controllers are used with condensable vapors. They are heated to prevent condensation of the vapors in the control system.

Mass flow controllers are often used to mix gases either outside the deposition chamber or in the deposition chamber. Again the getter-pumping action in the chamber prevents the MFM from giving a correct indication of the reactive gas availability in the chamber and some type of in-chamber monitoring technique is needed. This in-chamber gas composition monitoring can be done with a differentially-pumped mass spectrometer or by an optical-emission spectrometer if a plasma is used. A problem with these types of monitors is that they only analyze the gas mixture at a certain place in the chamber and variations with position are difficult to determine. For reproducible processing, the mass flow of each of the constituent gases and the total chamber pressure should be measured.

3.5.9 Fail-Safe Designs

Interlocks monitor some parameters and when a parameter falls outside of the parameter "window" a specific action is initiated generally through a microprocessor. For example, loss of water flow can result in the loss of cooling and allows overheating of some types of pumps and vaporization sources. Flow meters, temperature monitors, and flow switches can be used to detect the loss of water flow and to initiate the appropriate action. Vacuum switches can be used to detect pressure buildup in the processing chamber above a certain pressure level and initiate an action.

Vacuum switches can be used to prevent the high voltage from being applied when the system is not under vacuum. Interlocks should be placed on all electrical equipment to prevent untrained persons from having casual excess.

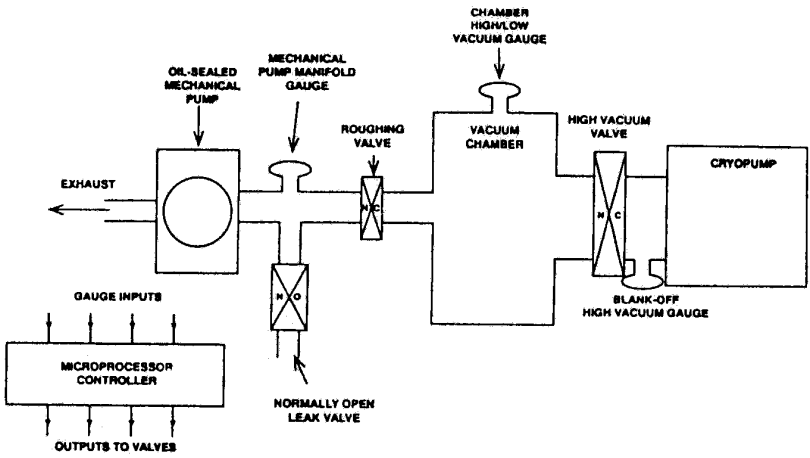
Systems should be designed so that in the event of an operator error or the failure of a critical system such as power, water, compressed air, cooling, etc. the system shuts down safely without contaminating the system, i.e. a fail-safe design. For example, oil sealed and oil lubricated mechanical pumps are commonly used to reduce the gas pressure in a deposition chamber to the range of 100 mTorr. An important factor in using these pumps is to minimize the "backstreaming" and "wall creep" of the mechanical pump oils into the deposition chamber and high vacuum pump. If oil migrates into the deposition chamber it can contaminate the substrate surface before film deposition or be decomposed in a plasma to deposit contaminants such as carbon. If the oil migrates into a cryopump it will fill the pores of the adsorbing media and decrease the pumping speed and capacity. If the low-temperature hydrocarbon oil migrates into an oil diffusion pump the high vapor pressure mechanical pump oil will quickly make its way into the deposition chamber.

One source of backstreaming is when there is a power failure and the mechanical pump stops. The oil seal in the pump is not effective in holding a large pressure differential and air will "suck" back through the pump carrying oil with it into the pumping manifold. In order to prevent this oil contamination an orifice or ballast valve on the roughing pump manifold provides a continuous gas flow through the mechanical pump even when the roughing and foreline valves are closed so as to keep the manifold pressure in the viscous flow range. In the event of a power failure, this leak brings the pumping manifold up to ambient pressure thereby preventing air (and oil) from being sucked back through the mechanical pump. This permanent leak in the roughing manifold adds a pumping load to the mechanical pump which must be allowed for in the system design. If such a permanent leak is not used, then a normally-open (NO) (when power is off) "leak-valve," which opens when there is a power failure, can be used in the manifold between the mechanical pump and the roughing valve.

The roughing, backing, and high vacuum valves should be pneumatic or solenoid operated, normally-closed (NC) (when power is off) valves, which will close on power failure and not reopen until the proper signal is sent from the microprocessor. The roughing valve and backing valve are activated from a preset vacuum signal to prevent lowering the

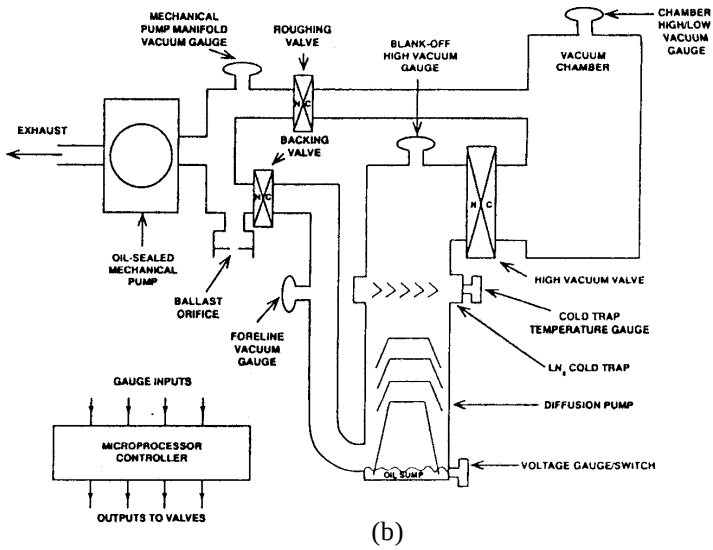
manifold pressure below the viscous flow range. It is also advisable to have the microprocessor programmed so that the roughing valve will not open if the pumping manifold is at a much higher pressure than the high vacuum side of the valve. For example, if there is a short power outage the roughing manifold will be brought to ambient pressure through the permanent leak or the actuated leak-valve, but the diffusion pump and/or the vacuum chamber can remain under a good vacuum. If power returns and the roughing valve or backing valve opens, then the gas flow will be reversed and gas will flow from the mechanical pump manifold into the high vacuum pump.

Figure 3-15 shows ways that the vacuum manifolding can be designed to "fail-safe" and minimize oil contamination from the mechanical pumping system when used with a diffusion-pumped system and a cryopumped system. In the diffusion pumped system, the diffusion pump can be interlocked so as to not heat up until the liquid nitrogen (LN2) cold trap has been cooled. Also shown in the figures is a high vacuum gauge between the high vacuum pump and the high vacuum valve. This gauge allows monitoring the status of the pumping system in a "blanked-off" mode. A major change in the pump performance in the blanked-off mode indicates a problem in the pumping system such as oil contamination of a cryopump, a low oil level in the oil-sealed mechanical pump, a low oil level in the diffusion pump, an incorrect oil sump temperature in the diffusion pump, etc.



(a)

Figure 3-15. Fail-safe designs for use with (*a*) cryopumped system, (*b*) diffusion pumped system (see next page).



(b)

Figure 3-15 cont.

"What-If" Game

In order to identify possible modes of failure and be able to design in safeguards you should play the "what if game." List all the things that could go wrong from power failure (both short-term and long-term) to operator error to loss of coolant flow. Determine what effect this would have on the system and process and try to design the system or operating procedures to avoid the problem. Some of the scenarios are:

- Power goes off for a long period of time (things cool down)
- Power goes off momentarily (things don't cool down)
- Coolant loss
- Air pressure loss (affects pneumatic valves)
- Exhaust line is plugged
- Valve cannot close because it is jammed
- Brown-out (voltage decrease)

3.6 VACUUM PUMPING

A vacuum is produced in a processing chamber by a combination of vacuum pumps. An important concept in vacuum pumping is that the molecules are not actually attracted by the pump but rather that they move freely through the system until they, by chance, find a pump which "traps" them or provides them with a preferential flow direction. Thus a vacuum pump is a device that takes a gas or vapor atom/molecule that enters it and prevents it from returning to the processing chamber.

The pressure in the vacuum system is partially reduced ("roughed") by rapidly evacuating the system using high-throughput mechanical pumps or in some cases is partially "roughed" using a large-volume evacuated ballast tank. The speed used to rough the system down can vary greatly. A rapid roughing time can allow a rapid cycle time. However rapid roughing can "stir-up" particulates in the system and does not allow time for vapors to be desorbed from surfaces. If this is a problem the roughing speed can be decreased to give a low flow rate at the pumping port. In order to reduce the roughing speed, a "soft-start" valve can be used with its conductance programmed to increase as the pressure decreases.

A vacuum pump may operate by:

- Capture, compress and expel the gas molecules (positive displacement pump), e.g. mechanical pump
- Give the gas molecule a preferential direction (momentum transfer pump), e.g. diffusion pump, turbomolecular pump, aspiration pump, vacuum cleaner
- Capture and keep the gas molecules (adsorption pump, absorption or reaction pump), e.g. cryopump, sorption pump, ion pump, evaporative getter pump, absorption pump, getter pump

3.6.1 Mechanical Pumps

Mechanical pumps are positive displacement pumps that take a large volume of gas at low pressure and compress it into a smaller volume at higher pressure. Some mechanical pumps can be used as air compressors. The earliest vacuum pumps were mechanical pumps. Gaede developed a mechanical pump in 1905 that is very similar to the oil-sealed rotary vane pumps used today. Many mechanical pumps have multiple stages

operating from a common motor and shaft. Mechanical pumps can be either belt-driven or direct-drive. Some direct-drive pumps may be disassembled by separating the pump from the motor leaving the manifolding on the system—this is particularly useful when pumping hazardous gases where the pumping manifold should stay sealed while changing the motor.

Mechanical pumps are often used to "back" high vacuum pumps and the pump capacity should not be restricted by the conductance between it and the high vacuum pump or by the conductance of the exhaust system. Many of the mechanical pumps can exhaust to ambient pressure whereas most high vacuum pumps cannot. The mechanical pump is connected to the high vacuum pump using a foreline manifold. The foreline pressure of the diffusion-type high vacuum pump is an important factor in contamination control. If it is too high, backstreaming occurs from the diffusion pump into the processing chamber. If it is too low, backstreaming occurs from the mechanical pump into the diffusion pump.

Oil-Sealed Mechanical Pumps

The most common mechanical pumps are the oil-sealed mechanical pumps, such as the rotary vane pumps, and the "dry" blower pumps as shown in Fig. 3-16.[79] These pumps are used when high volumes of gas must be pumped. When oil-sealed mechanical pumps are used with chemicals, or particulates are formed in the processing, oil filtration systems should be used. These filter out particulates and neutralize acids in the oil. The oil can be cooled during circulation. Many mechanical pumps are equipped with a ballast valve to allow the introduction of diluent gases (e.g. nitrogen) directly into the pump intake. These diluent gases reduce the partial pressure of corrosive or condensable gases and vapors. When pumping corrosive materials, the internal parts of the pumps may become corroded and the internal surfaces should be continuously coated with oil by splashing action—this may be achieved by having a high gas throughput using the ballast valve. Also the pump should be run hot in order to volatilize material in the oil. Contaminant fluid in the pump oil degrades the performance of the pump to the point that the lowest pressure attainable is the vapor pressure of the contaminant fluid. Fluids in the oil may also cause frothing which presents sealing problems in oil-sealed pumps.

Many mechanical pumps use hydrocarbon oils for sealing. When pumping reactive chemical species, hydrocarbon oils may be easily degraded. The perfluorinated polyethers (PFPE) which only contain fluorine, oxygen

and carbon, may be used to provide greater chemical stability.[80] When using this type of oil, the mechanical pump may have a sump heater to decrease the viscosity of the oil, particularly for start-up. These pump oils have inferior lubricating properties compared to the hydrocarbon oils.

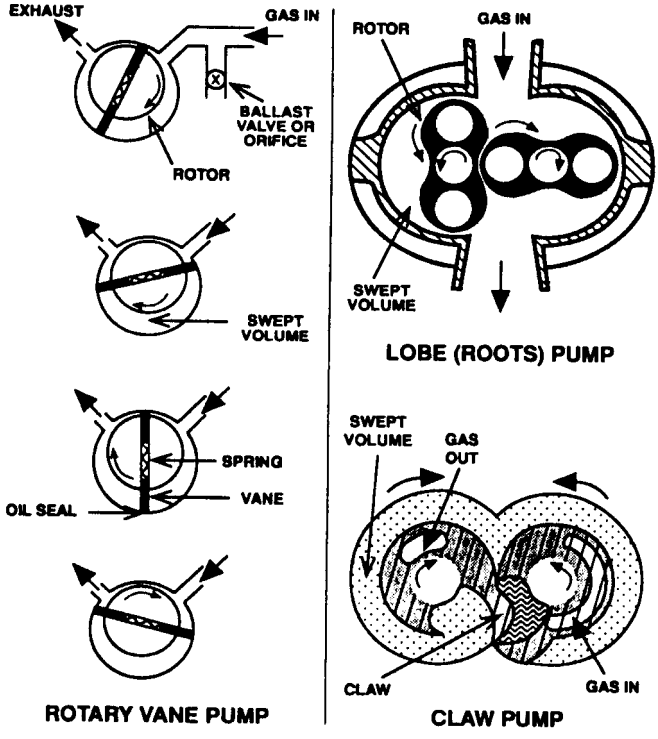


Figure 3-16. Oil-sealed and "dry" mechanical pumps.

Compression of pure oxygen in contact with hydrocarbon oils, may cause an explosion. When using oxygen, either less-explosive gas mixtures, such as air, should be used or a ballast valve or ballast orifice should be used to dilute the gas mixture to a non-explosive composition. Alternatively an oxidation-resistant pump oil can be used.

Dry Pumps

Oil-free (relatively) or dry pumps have been developed to meet the needs of processes that generate particulates or reactive species that

degrade the pump oils.[81]-[85] In addition, they are relatively oil-free thus avoiding the potential of oil contamination in the deposition system. Dry pumps are more tolerant of particulates than are the oil-sealed mechanical vane pumps. They can have gas injection ports to allow purge gases to be introduced to aid in sweeping particulates through the pump. Generally dry pumps are noisy and bulky.

The most common dry pumps are single or multistage Roots blowers and "claw" blowers.[86][87] Pumping packages consisting of a blower backed by a mechanical pump capable of flow rates of 10,300 cfm are available. A screw-type dry pump allows pumping from 4 mTorr to atmosphere with one stage. A scroll pump uses an orbiting action to compress the gas; it has a better ultimate than does the oil-sealed mechanical pump. The multistage piston pump is similar in construction to a gasoline engine.

Diaphragm Pumps

The diaphragm pump is a dry pump that compresses the gases (or fluids) by a flexing diaphragm, and can be used when the gas load is not too high.[88] Some diaphragm pumps have an efficient pumping range of atmospheric to 10 Torr with a gas throughput of 1.5 liters/sec or so and an ultimate vacuum of 10^{-6} Torr. The diaphragm pump can be used to back a molecular drag pump or a turbomolecular pump with molecular drag stages making a relatively oil-free pumping system for low throughput requirements such as leak detectors and some load-lock modules.

3.6.2 Momentum Transfer Pumps

Diffusion Pumps

The diffusion pump (DP) or vapor jet pump is a momentum transfer pump that uses a jet of heavy molecular weight vapors to impart a velocity (direction) to the gases by collision in the vapor phase as shown in Fig. 3-17[89] and is probably the most widely used high vacuum pump in PVD processing. The pump fluid is heated to an appreciable vapor pressure and the vapor is directed toward the foreline by the vapor-jet elements of the diffusion pump. If the high vacuum valve is opened when the processing chamber pressure is too high, the vapor jet does not operate effectively

("overloading") and backstreaming into the processing chamber can occur.[89a] Reference should be made to the manufacturer's pump data sheet for the maximum allowable foreline pressure. This should be the optimum "crossover pressure" for changing from the rough pumping system to the high vacuum pumping system.*

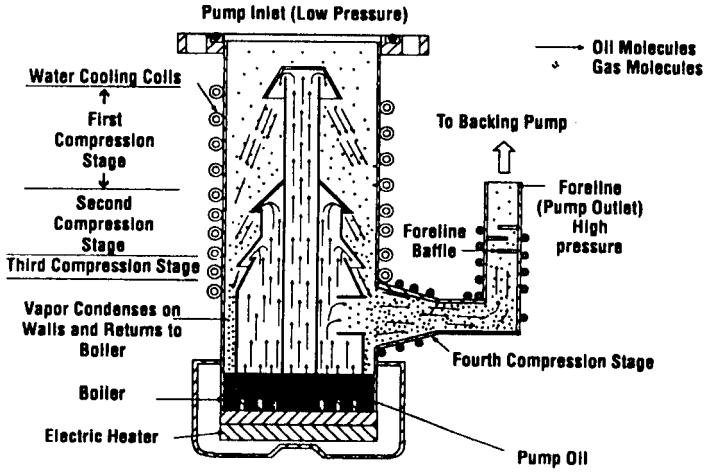


Figure 3-17. Oil diffusion pump.

Important oil diffusion pump operating parameters are:

- Oil sump temperature—depends on the pump oil
- Oil level

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*An engineer had the problem that sometimes he could not get molten aluminum to wet the stranded tungsten filament in a vacuum deposition process. Questioning revealed that an oil-sealed mechanical pump was being used for roughing and the crossover over from roughing to high vacuum pumping was at about 10 microns. This is well within the molecular flow range of his roughing system plumbing allowing backstreaming from the oil-sealed mechanical pump into the deposition chamber. The problem was that on heating the tungsten filament, the hydrocarbon oil on the filament "cracked" forming a carbon layer which the molten aluminum would not wet. The oil was probably also degrading the cryopump that was being used for high vacuum pumping. The system was cleaned and the crossover pressure was raised to 100 mTorr and the problem went away.

- Upper pump housing temperature
- Foreline pressure
- Processing chamber pressure

These parameters should be continuously monitored or periodically checked.

The hydrocarbon lubricating and sealing oils used in mechanical pumps must not be allowed to backstream or creep to the diffusion pump and contaminate the diffusion pump oil!!!! Power failure, cooling failure, or mistakes in operating a diffusion pumped system can result in pump oil contaminating the processing chamber. In some applications, cryopumps or turbopumps are used instead of diffusion pumps to avoid the possibility of oil contamination.

Diffusion pump fluids are high molecular weight material, such as many oils and mercury, that vaporize at a reasonable temperature. A concern is the thermal and chemical stability of the fluid. Hydrocarbon oils tend to breakdown under heat to form low molecular weight fractions, or they may oxidize and polymerize into a varnish-like material and therefore are not desirable for many applications. Silicone oils are much more stable with respect to temperature and oxidation and are the fluids most often used for vacuum deposition processes. When pumping very reactive chemical species, such as is used in plasma etch or PECVD processing, an even greater stability is desired and this is found with the perfluorinated polyethers (PFPE) which only contain fluorine, oxygen and carbon.[80]

In order to minimize backstreaming in a high vacuum pumping stack, cold baffles are used as optical baffles between oil-containing pumps and the processing chamber. The cold surfaces condense vapors. The surfaces are generally cooled by liquid nitrogen although sometimes refrigerants are used.[89a] The cold baffle should be placed between the pump and the high vacuum valve and should always be cold when the vacuum pumps are running and before the high vacuum valve is opened. Oil, particularly silicone oil, from pumping systems may creep along a wall to the processing chamber. Wall creep may be minimized by having a cold region or non-wetting surface on the vacuum plumbing between the pump and the processing chamber.

Turbomolecular Pumps

The turbomolecular pump or "turbopump" is a mechanical type momentum transfer pump in which very high speed vanes impart momentum to the gas molecules as shown in Fig. 3-18.[90] This type of pump operates with speeds up to 42,000 rpm. Pumping speeds range from a few liters/sec to over 6500 liters/sec. Turbopumps require very close tolerances in the mechanical parts and cannot tolerate abrasive particles or large objects. In some pumps, metallic or ceramic ball bearings are replaced by air bearings or magnetic bearings, to avoid oil lubricants which can be a source of contamination. Turbopumps operate well in the range 10^{-2}–10^{-8} Torr.

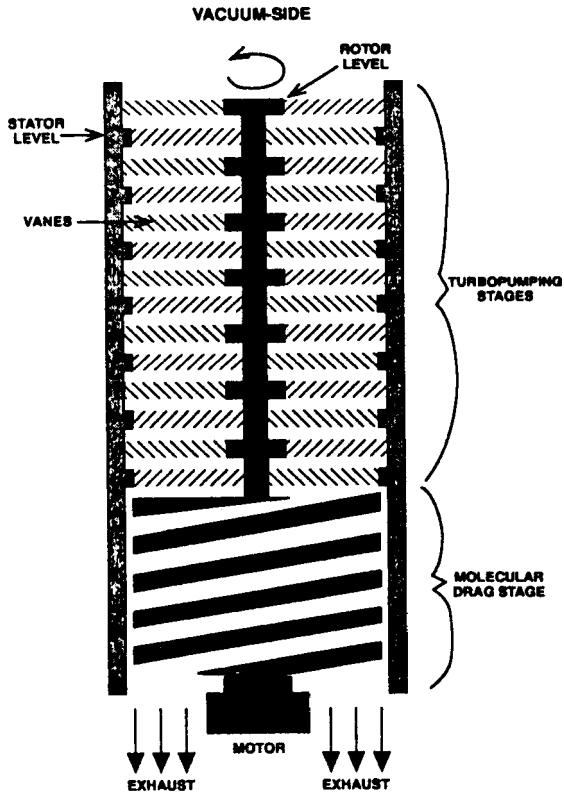


Figure 3-18. Turbomolecular pump with a molecular drag stage.

Turbopumps have compression ratios of 10^9 for nitrogen and 10^3 for hydrogen and they are most often backed with a mechanical pump. Turbopumps are sometimes used with no high vacuum valves but are rough-pumped through the turbopump as it is accelerating. When used to pump corrosive gases, the metal surfaces must either be made of a non-corrosive material or coated with a non-corrosive material and the bearings must be non-metallic or protected with inert gas shields. Turbopumps have poor pumping ability for water vapor since the water molecules must make many adsorption-desorption events to pass through the pump.

In many turbopumps the first stage is a rotating stage that is exposed to the vacuum chamber. This stage is usually protected by a screen to prevent items from striking the rotating blades. In reactive deposition processes utilizing carbon from hydrocarbon precursor gases, this screen can become coated by particulates and the pumping speed reduced dramatically. The screen should be cleaned periodically.

Molecular Drag Pumps

The molecular drag pump uses a high velocity surface to "drag" the gas in a given direction.[90] The molecular drag element can be in the form of a disk (Gaede-type) or a cylinder with a spiral groove (Holweck-type). The molecular drag pump has an efficient pumping range of 1–10^{-2} Torr and an ultimate in the 10^{-7} Torr range. An advantage of the molecular drag pump is that it has a high compression for light gases, it is oil-free and can be exhausted to a higher pressure (10 Torr) than a turbopump. This pump has some advantages in helium leak detection pumping in that it can easily be flushed and used in a "counterflow" (backstreaming) mode that eliminates the use of throttling valves.[91][92] For very clean applications, the molecular drag stage is backed by an oil-free pump. This type of pumping system is used in semiconductor load-locks, mass spectrometers, leak detectors and for pumping corrosive gases.

3.6.3 Capture Pumps

Sorption (Adsorption) Pumps

Sorption pumps are capture-type pumps in which the gases are adsorbed on activated carbon, activated alumina, or zeolite surfaces in a

container that is cooled directly, generally by immersion in liquid nitrogen.[90][91] The adsorption of gases not only depends on the temperature and pore size of the adsorbing media but also on the gas pressure and the amount of gases already adsorbed. The pump works best for pumping nitrogen, carbon dioxide, water vapor and organic vapors. It works poorly for pumping helium. Ultimate pressures of 10^{-3} Torr are easily obtained when pumping air with these pumps. These pumps are often used to rough clean systems where the potential for contamination by a mechanical pump is to be avoided. Several sorption pumps may be used sequentially to increase pumping speed and effectiveness. After absorbing a significant amount of gas, the pumps must be regenerated by heating to room temperature if the adsorbing medium is carbon or to 200°C if the adsorbing medium is a zeolite.

Activated carbon is an amorphous material with a surface area of 500–1500 m^2/gram. It has a higher efficiency for adsorbing non-polar molecules than for polar molecules. For adsorbing gases a pore size of 12–200 Å is used. Activated carbon has a high affinity for the absorption of organic molecules and is used to adsorb organic molecules from fluids. For this application, a carbon having a pore size of 1000 Å is used. After cryosorbing gases, the carbon adsorbers desorb the trapped gases ("regenerated") on being heated to room temperature.

Zeolites are alkali alumino-silicate mineral materials which have a porous structure and a surface area of 10^3 m^2/g. The zeolite materials are sometimes called molecular sieves because of their adsorption selectivity based on pore size. The material can be prepared with various pore opening sizes (3Å, 5Å, 13Å) with 13Å material, such as the Linde molecular sieve 13X, being used in sorption pumps. The 13Å pore is about the diameter of the water vapor molecule. Smaller pores can be used to selectively absorb small atomic diameter gases but not large molecules. One gram of the 13X zeolite absorbs about 100 mTorr-liters of gas. Zeolites materials are also used in foreline traps, either cooled or at room temperature, to collect backstreaming organic vapors. The zeolites must be "regenerated" by heating to about 200°C to remove adsorbed water. Large molecules, such as oils, will plug the pores and render the zeolites incapable of adsorbing large amounts of gas.

Cryopanels

Cryopanels are cryocondensation surfaces in the deposition chamber that use large areas of cooled surfaces to "freeze-out" vapors, particularly

water vapor and solvent vapors.[91a] They are cooled by liquid nitrogen at -196°C or refrigerants to about -150°C, from a closed-cycle refrigerator/ compressor system. The vapor pressure of water at these temperature is very low as shown in Table 3-4. It takes about 780 watts to freeze one kilogram of water per hour and eleven kilograms of liquid nitrogen to freeze one kilogram of water. The ideal cryosurface should pump about 10 liters per second per square centimeter.

As ice forms on the panel surface, the thermal conductivity to the cold surface is decreased. This ice must be periodically removed by warming the surface. For this in-chamber type of cryocondensation, it is important that the pumping surface not be heated by heat generated during processing!!!! A major advantage of the cryopanel is that it can custom designed and placed in the processing chamber so the conductance to the surface is high.

Cryopumps

A cryopump is a capture-type vacuum pump that operates by condensing and/or trapping gases and vapors on several progressively colder surfaces.[90] Figure 3-19 shows a schematic of a cryopump. The coldest surfaces are cooled by liquid helium to a temperature of 10–20 K (-263 to -253°C) which solidifies gases such as N_2, O_2, and NO. Gases which do not condense at temperatures of 10–20 K, such as He, Ne, H_2, are trapped by cryosorption in activated charcoal panels bonded to the cold elements. Other surfaces are near the temperature of liquid nitrogen (77 K or -196°C) which will solidify and cool vapors, such as water and CO_2, to a temperature such that their vapor pressure is insignificant. Most gases are condensed in a cryopump and the pumping speed is proportional to the surface area and the amount of previously pumped gas on the surface. Cryopumps have the advantage that they can be mounted in any position. The helium compressor/refrigeration unit for the cryopump can be sized to handle the requirements of several cryopumps.

The pumping speed of a cryopump is very high in comparison with other pumps of comparable size. The best vacuum range for the cryopump is 10^{-3}–10^{-8} Torr. The cryopumpimg speed varies for different gases and vapors. For example the pumping speed may be 4200 liters/sec for water vapor, 1400 liters/sec for argon, 2300 liters/sec for hydrogen, and 1500 liters/sec for nitrogen. The cryopump has a specific capacity for various gases. The pumps are rated as to their gas capacity at a given

pressure. For example, at 10^{-6} Torr for a 20" cryopump, the capacity might be 10,000 standard (760 Torr and 0°C) liters of argon, 27,500 standard liters of water vapor, and 300 standard liters of hydrogen. The capacity for condensable gases is much higher than that for trapped (cryosorbed) gases with the hydrogen capacity generally being the limiting factor. When the gas capacity for one gas is approached, the pump should be regenerated in order to achieve maximum performance.

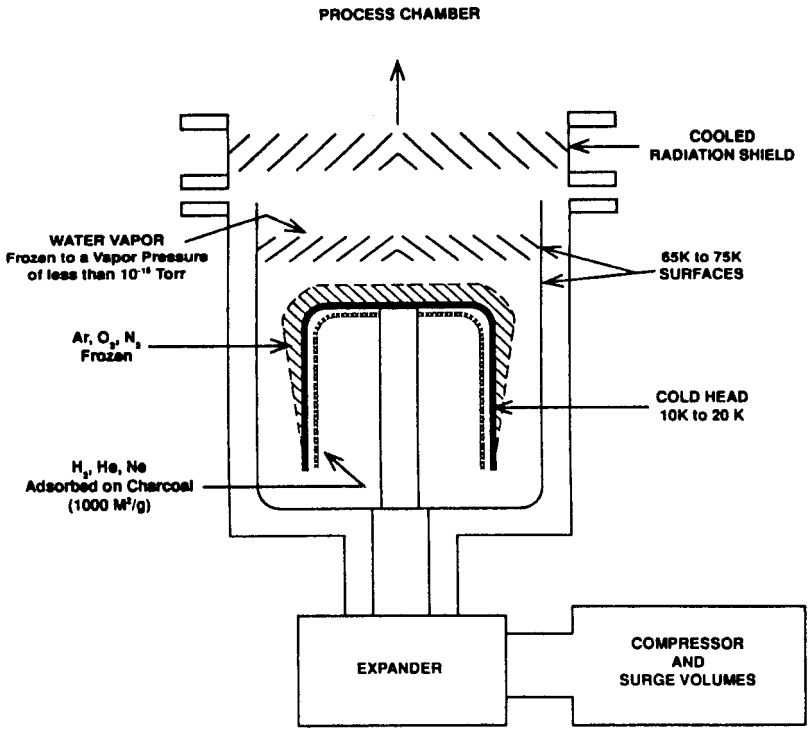


Figure 3-19. Cryopump.

Regeneration of the pump can be accomplished by allowing it to warm up to room temperature and purging with a dry heated gas. A typical regeneration cycle with a cryopump used in sputter deposition, might be once a week with the regeneration time requiring several hours. Recently, a cryopump has been introduced that can selectively regenerate the 10–20 K surfaces and thus reduce the regeneration time to less than an hour.

The worst enemy of cryopumps are vapors, such as oils, that plug-up the pores in the cryosorption materials and do not desorb during

the regeneration cycle. Cryopumps should never be used to pump explosive, corrosive, or toxic gases since they are retained and accumulate in the system. The cryopump is very desirable for non-contamination requirements such as in critical thin film deposition systems. The internal pump design determines the cool-down time, sensitivity to gas pulses, and the ability of the cryopump to be used with high temperature processes. In processing applications, care should be taken that the pump elements are not heated by radiation or hot gases from the process chamber. For example, in thermal evaporation, the cryopumps may produce a "burst of pressure" when the evaporation is started because the pump is not adequately shielded from radiant heating from the thermal vaporization source.

Cryopumps are very useful when very clean pumping systems are desired. However if pumping water vapor is the concern, then an in-chamber cryopanel may be a better answer since the conductance to the cold panel for water vapor can be made very high.

Getter Pumps

The getter pump is a capture-type pump that functions by having a surface that chemically reacts with the gases to be pumped or will absorb the gases into the bulk of the getter material. The reactive surface can be formed by continuous or periodic deposition of a reactive material such as titanium or zirconium or can be in the form of a permanent solid surface that can be regenerated.[95][96] These types of pumps are typically used in ultraclean vacuum applications to remove reactive gases at high rates. The ion (sputter-ion) pump uses sputtering to provide the gettering material. It is mostly used for UHV pumping of small volumes. In many instances their use is being supplanted by the super-clean combination of a hybrid turbomolecular/molecular-drag pump backed by a diaphragm pump.

In some PVD deposition configurations, the material that is evaporated or sputtered can be used to increase the pumping rate in the deposition chamber. This effect can be optimized by proper fixture design so as to make any contaminant gases or vapors strike several freshly deposited gettering surfaces before they can reach the depositing film. Getter pumping is an important factor in reactive PVD where the depositing film material is reacting with the gaseous environment to form a film of a compound material, i.e. getter pumping the reactive gas. For example, if titanium nitride (TiN) is being deposited over 1000 cm^2 of surface area at 10 Å/sec it will be getter-pumping about 90 sccm (1.14 Torr-liters/sec) of

nitrogen gas in the deposition chamber. This in-chamber pumping reduces the partial pressure of the reactive gas during processing and changes the availability of the reactive gas. The amount of in-chamber pumping will depend on the area over which the film is being deposited and the deposition rate. Thus it will make a difference as to how much surface area is being deposited ("loading factor"). Deposition rate will also be a factor.

3.6.4 Hybrid Pumps

Various type of pumps can be combined into one pump to create a hybrid pump. For example, molecular drag stages can be added to the shaft of a turbomolecular pump and such a combination pump can be run from 10^{-9} Torr inlet pressure to several Torr exhaust pressure with a constant pumping speed and a high compression (10^{11}) for light gases (nitrogen).[97][98] These "hybrid" or "compound" pumps can be backed by diaphragm pumps. Such a combination can be backed by a diaphragm pump producing a super-clean pumping system that is used on load-locks, leak detectors, and for long-term vacuum outgassing systems where high pumping speeds are not a requirement. A cryopump can be combined with a turbo pump to increase the pumping speed for water vapor.

3.7 VACUUM AND PLASMA COMPATIBLE MATERIALS

Vacuum-compatible materials are those that do not degrade in a vacuum and do not introduce contaminants into the system. For example, carbon motor brushes that operate well in air, disintegrate rapidly in vacuum due to the lack of moisture. Plasma-compatible materials are ones that do not degrade in a plasma environment. For example, oxidizing plasmas (oxygen, nitrous oxide) rapidly degrade oxidizable materials such as polymer gaskets. Chlorine-containing plasmas rapidly corrode stainless steel. Inert gas plasmas emit ultraviolet radiation that can degrade polymer materials. In PECVD and plasma etching, hot corrosive reaction products can degrade materials and components downstream from the reaction chamber. Materials should be characterized as to their vacuum/plasma/process compatibility prior to being incorporated into a processing system.

Materials with potentially high vapor pressure constituents should be avoided in a vacuum system even though they might be usable. Examples are:

- Brass (Cu : 5–40% Zn) releases zinc at temperatures greater than 100°C. Brass may be electroplated with copper or nickel for better vacuum compatibility. Bronze (Cu : 1-20 % Sn) has many of the same machining properties as brass but is more expensive. A typical bronze is bell-bronze (77% copper, 23% tin). Copper-beryllium (Cu : 2 % Be) is much harder than brass.
- Cadmium plated bolts—the cadmium vaporizes easily and the cadmium should be stripped before they are used.

Note: Cadmium plating can be stripped by a short immersion at room temperature in a solution of: concentrated HCl (2 liters) + Sb_2O_3 (30 g) + deionized water (500 ml).

3.7.1 Metals

Metals are normally used for structural materials in vacuum systems. Stainless steel is the most commonly used material for small vacuum chambers. Mild steel is often used for large chambers. Atmospheric pressure exerts a force of about 15 psi on all the surfaces, so vacuum chamber walls must be able to withstand that pressure without failure or unacceptable flexure. Material thickness should satisfy ASME Boiler and Pressure Vessel Code requirements. Bracing may be necessary on large-area surfaces to prevent deflection. Beware of porosity and microcracks in the material which can cause leaks through the wall. Porosity in steel is often caused by sulfur stringers. Porosity in small steel pieces can generally be avoided by using vacuum melted and forged material. In large steel chambers the porosity is often plugged by painting the exterior of the chamber. Aluminum seldom has problems with porosity. Microcracking can be due to deformation of the metal during fabrication and is compounded by using materials with high inclusion content.

Machining of metals should be done so as to prevent smearing and trapping of contaminants in the surface—this means using a sharp tool with a light finish cut. Aluminum in particular tends to "tear" if machined improperly. Typically the surface should have a 0.813 micron (32 microinch) R_a finish after machining. The surface can then be chemically-polished

or electropolished to a 0.254 micron (10 microinch) R_a or better finish. When using large plates, it may be necessary to relieve the stress in the plate by heat treatment before welding or machining to minimize warping.

Stainless Steel

One of the most commonly used corrosion-resistant metals in vacuum engineering is stainless steel. Stainless steel is generally desirable in that it will reform its surface oxide when the oxide layer is damaged. There are many stainless steel alloys such as:

- 304 common machinable alloy, non-magnetic—beware of carbide precipitation in weld areas which can cause galvanic corrosion (pitting).
- 304L (low carbon)—used for better intergranular corrosion resistance than is obtained with 304. Used for fluid lines and gas lines containing moisture.
- 316 for general corrosion resistance—do not mix 304 and 316 when used in fluid transport because of galvanic corrosion at joints.
- 316L—better intergranular corrosion resistance. The chemical analysis (%) of 316L is typically C = 0.035 max, Cr = 16-18, Ni = 10-15, Mn = 2 max, Si = 0.75 max, P = 0.040 max, S = 0.005-0.017 max, Mo = 2-3.
- 303 has a high sulfur content and a higher tendency for porosity. This material is not recommended since it cannot be welded very well.
- 440—hardenable, magnetic and more prone to corrosion than the 300 series.

Stainless steels are available as mill plate with several finishes:

- Unpolished #1—very dull finish produced by hot-rolling the steel followed by annealing and descaling. The surface is very rough and porous. This material is used where surface finish and outgassng are not important.
- Unpolished #2D—Dull finish produced by a final cold roll after the hot rolling but before annealing and

descaling. Used for deep drawing where the surface roughness retains the drawing lubricant.

- Unpolished #2B—Bright finish obtained by a light cold roll after annealing and descaling. Grain boundary etching due to descaling still present. General purpose finish.
- Polished #3—Intermediate polish using 50 or 80 grit (Table 12-1) abrasive compound. R_{max} of 140 microinches (3.5 microns). Heavy polishing grooves.
- Polished #4—General purpose surface obtained with 100–150 grit abrasives. R_{max} of 45 microinches. Lighter polishing groves.
- Buffed #6—Polished with 200 grit abrasive.
- Buffed #7—Polished with 200 grit abrasive with a top-dressing using chrome oxide rouge. R_a of 8-20 microinches.
- Buffed #8—Polished with 320 grit abrasive (or less) with an extensive top-dressing using chrome oxide rouge. R_a of 4-14 microinches. To the eye the surface appears to be free of grinding lines.

The surface of stainless steel can be chemically polished or electropolished to make it more smooth. Electropolishing[99] decreases the R_a by about a factor of two as well as acts to eliminate many of the microcracks, asperities and crevices in the polished surface. Typically electropolishing is done in an electrolyte containing phosphoric acid and the smooth areas are protected by a thin phosphate layer causing the peaks to be removed. This phosphate layer should be removed using an HCl rinse and then the surface rinsed to an acid-free condition prior to use. Directed streams of electrolyte ("jets") can be used to selectively electropolish local areas of a surface.[100] Commercial suppliers provide electropolishing services to the vacuum industry either at their plant or on-site at the customer's plant.

Electropolishing decreases the surface area available for adsorption and reduces the contamination retention of the surface. The electropolished surface generally exhibits a lower coefficient of friction than a mechanically polished surface. The various surface treatments can alter the outgassing properties of the stainless steel surface.[41][101]-[104] The chemical composition of and defect distribution in electropolished surfaces can be

specified for critical applications.[105][106] This includes the chromium-to-iron ratio with depth in the oxide layer (AES), the metallic and oxide states (XPS), surface roughness (AFM), and surface defects (SEM).

Electropolishing, as well as acid treatments, "charge" the steel surface with hydrogen, and for UHV applications the stainless steel should be vacuum baked at 1000°C for several hours to outgas hydrogen taken up by the surface. The surface of stainless steel will form a natural passive oxide layer 10-20Å thick when dried and exposed to the ambient.

The surface of stainless steel can be passivated by heating in air. However, the temperature and dew point are very important. A smooth oxide film is formed on 316L stainless steel at 450°C and a dew point of 30°C but small nodules and surface coarsening result when the oxidation is done above 550°C in air with this dew point.[107][108] These nodules can produce particulate contamination in gas distribution systems and the coarse oxide adsorbs water vapor more easily than does the smooth dense oxide. If the dew point of the air is lowered to -100°C, then a smooth oxide with no nodules is formed at higher temperatures. For example a four hour oxidation of electropolished stainless steel at 550°C and a dew point of -100°C produces a 100–300 Å thick oxide compared to the 10–20 Å thick natural oxide found on the electropolished surface with no passivation treatment. Type 304 and 316 stainless steels are more easily passivated than are the 400 series (hardenable) stainless steels.[109] The stainless steel surface can be chemically passivated using organosilanes which form a hydrophobic surface layer on the stainless steel.[74] The organosilanes also aid in removing water from the distribution lines by chemically reacting with the water during their deposition.

The oxide formed on stainless steel is electrically conductive. Stainless steel has a poor thermal conductivity and should not be used in applications requiring good thermal conductivity. Welding of stainless steel can affect the corrosion resistance in the "heat affected zone" (HAZ). This can be controlled by limiting the amount of carbon in the material to minimize formation of chromium carbide and by using special passivation procedures.[110]

The 300 series stainless steel can be work hardened during fabrication (such as machining shear flanges) but the material anneals (softens) at about 450°C. Stainless steel will gall and seize under pressure, particularly if the surface oxide is disturbed. Threads on stainless steel should be coated with a low-shear, anti-seize material such as silver, applied by electroplating or ion plating, or a molybdenum disulfide-containing lubricant applied by burnishing.

Low-Carbon (Mild) Steel

Low carbon steel or mild steel, is an attractive material for use in large vacuum systems where material costs are high. This type of steel often has porous regions but painting with an epoxy paint will seal the surface. Painting is usually on the exterior surface but is sometimes on the interior surface. Low-outgassing-rate paints are available for vacuum applications. Care should be taken that the steel on the vacuum surfaces and on the sealing surfaces does not rust. Small amounts of rust can be removed with a sodium citrate solution (1 part sodium citrate to 5 parts water) without affecting the base metal. If the oxide on the steel is removed, the surface can be protected by a "rust preventative." In the case of O-ring seals to mild steel surfaces, it is recommended that the O-rings be lightly greased before installation.

Carbon steel and low alloy steels may be cleaned by electroetching or by pickling in a hydrochloric acid bath (8–12 wt %) at 40°C for 5–15 min. to strip the oxide from the surface.[111]

A simple technique to remove iron rust is as follows:

- Solvent clean
- Soak in fresh white vinegar (acetic acid)
- Brush away residue
- Repeat as necessary

Aluminum

Aluminum is an attractive metal to use as a vacuum material because of its ease of fabrication, light weight, and high thermal conductivity. However the natural oxide that forms on aluminum and thickens with time is rather porous and can give appreciable outgassing.[42] Mill rolled aluminum has an outgassing rate ~100 times that of mill rolled stainless steel.[112] Aluminum is not normally used for vacuum processing systems because it is soft and easily corroded.

With proper fabrication and handling, aluminum has proven to be a good high and ultra-high vacuum material when cleaned with care.[113] A dense thin oxide with good outgassing properties can be formed on aluminum surfaces by: (1) machining under an dry chlorine-free argon/oxygen gas, (2) machining under pure anhydrous ethanol, or (3) extrusion under a

dry chlorine-free argon/oxygen gas.[113]-[115] Aluminum can be polished by chemical polishing and electropolishing.

For shear or deformation sealing, the surface of the aluminum is usually hardened to prevent deformation of the sealing surfaces. This can be done by using an ion plated coating of TiC[116] or TiN on the sealing surfaces. Aluminum has a very high coefficient of thermal expansion and thin sheets of aluminum will warp easily if heated non-uniformly. Aluminum can be joined to stainless steel by electroplating or by explosive bonding.

In special cases where the surface hardness must be increased or chemical corrosion resistance is necessary (e.g. plasma etching with chlorine) anodized aluminum surfaces can be useful.[117] Alloying elements, impurities and heat treatment can influence the nature and quality of the anodized coating—typically the more pure the aluminum alloy, the better the anodized layer. To build up a thick anodized layer on aluminum, it is necessary for the electrolyte to continuously corrode the oxide producing a porous oxide layer. *ASTM Specification B-580-73* designates seven thicknesses (up to 50 microns) for anodization. Anodization baths for the various thicknesses are:

Oxalic anodize—very thick films (50 microns)

Sulfuric acid—thick films (80% aluminum oxide, 18% aluminum sulfate, 2% water—15% porosity)

Chromic acid—thin films (1–2 microns)

Phosphoric acid—very porous films (base for organic coatings)

After formation, the porous aluminum oxide can be "sealed" by hydration which swells the amorphous oxide. Sealing of sulfuric acid anodized surfaces is done in hot (95–100°C) deionized water, by using a sodium dichromate solution or by nickel or cobalt acetate solutions. Sealing reduces the hardness of the anodized film. Steam sealing can be used to avoid the use of nickel-containing hot water to prevent the possibility of nickel contamination in semiconductor manufacturing. For vacuum use, the anodized surface should be vacuum baked before use. To increase the corrosion protection or lubricity of the anodized surface, other materials can be incorporated in the porous surface. Examples are the "Magnaplate"™ coating to improve corrosion protection and "Tufram"™ coating used to improve the frictional properties of anodized aluminum surfaces.

Anodized aluminum does not provide a good surface for sealing with elastomer seals. In anodized systems the sealing surfaces are often

machined to reveal the underlying aluminum. These surfaces can be protected from corrosion with a thin layer of a chemically-resistant grease such as Krytox™.

Aluminum can be anodized with a dense oxide (barrier anodization)[118][118a] but this technique has not been evaluated for vacuum applications since the oxide that is formed is rather thin.

Copper

Copper is often used in vacuum systems as an electrical conductor or as a shear-sealing material. For corrosive applications the copper can be gold-plated.

Hardenable Metals

Wear and wear-related particle generation can be reduced by using metals with smooth, hard surfaces. Surfaces of some materials can be hardened and strengthened by forming nitride, carbide or boride dispersed phases in the near-surface region by thermal diffusion of a reactive species into the surface (Sec. 2.6.2).

3.7.2 Ceramic and Glass Materials

Ceramic materials such as alumina, boron nitride, silicon nitride, and silicon carbide are generally good vacuum materials if they are fully dense. However, they are sometimes difficult and expensive to fabricate in large shapes. Ceramics and glasses develop surface microcracks when ground or polished. These microcracks reduce the strength of the material as well as contribute to surface retention of contamination. Oxide ceramics and glasses can be etched in a solution of hydrofluoric acid or ammonium bifluoride which will mildly etch the surface and blunt the microcracks. Examples of special ceramic materials that can be used in a vacuum are:

- Macor™—machinable glass-ceramic composite
- Lava™ (synthetic talc)—machinable in "green" state and then "fired" to become a hard ceramic (there is approximately 12% shrinkage during firing).
- UCAR™—electrically conductive (TiB_2 + BN) ceramic
- Combat™ Boron Nitride—insulating, machinable

3.7.3 Polymers

The use of polymers should be minimized as much as possible in high vacuum applications because of outgassing problems. Polyvinyl-chloride (PVC) piping can be used for vacuum plumbing in applications where outgassing is not a problem such as exhaust lines and forelines. PVC can be bonded by heat-fusion, with a PVC cement or joined using demountable PVC "sanitary fittings" such as are used in the food industry.

3.8 ASSEMBLY

Subassemblies should be cleaned (and leak-checked) as thoroughly as possible before assembly so as to reduce the cleaning necessary on the final assembly. In particular salt residues should be avoided since they are deliquescent and will continuously take-up and release water. After final cleaning the vacuum surfaces can be conditioned (cleaned) to remove contamination.

3.8.1 Permanent Joining

Fusion welding is commonly used to join metals in the fabrication of structures. The welded joint should be designed so that there are no resultant virtual leaks in the vacuum chamber. This generally means that internal welds on deposition chamber walls are needed. Heating a carbon-containing stainless steel in the 600°C range causes the precipitation of chromium carbide at the grain boundaries. These carbides allow galvanic corrosion of the grain boundaries ("sensitization"). Low carbon stainless steels (e.g. 316L) should be used if the material is to be processed in that temperature range and used where electrolytes are present. Stresses may cause increased corrosion. Relief of the weld stresses in 304 stainless steel can be accomplished by heating to 450°C, and this improves the corrosion resistance of the weld areas.

The shrinkage of the molten weld material associated with welding may result in warping of the parts. Warping may be minimized by designing the weld joints so that only thin sections are welded along the neutral plane (midpoint of material thickness). Shrinkage of large molten pools may result in cracks and leaks and therefore the molten pool should be kept small. After

fusion welding of stainless steel, the joint should be passivated by the formation of an oxide layer and the removal of free iron, using nitric acid.

Structural welds should be made to ASME Boiler and Pressure Vessel Code requirements. Critical welds can be inspected using dye penetrants, ultrasonics, X-ray radiography, or by helium leak checking the joint. Welding sometimes leaves oxide inclusions in the weld region which may later open up giving a leak. It is important that the welds be well cleaned before leak checking.

Metals can also be joined by brazing. A braze material is one that melts at a temperature above 475°C. For vacuum applications the braze material should not contain high vapor pressure materials such as cadmium or zinc. Brazing is best performed in a vacuum environment ("vacuum brazing") to reduce chances for void formation and to use flux-less braze materials. Due to the high temperatures involved, the materials to be joined should have closely matched coefficients of thermal expansion, or "graded" joints should be used to prevent warping or stressing. Note that many braze alloys for brazing in air contain zinc or cadmium.

Glasses may be joined to metals and other glasses by fusion.[119] Often glass seals must be graded through several glass compositions from one material to another due to differences in their thermal coefficients of expansions. Ceramics may be metallized and then brazed to other ceramics or metals to form hermetic joints.[120] A ceramic-based adhesive that is capable of being used to 150°C is "Ceramabond™ 552." The adhesive cures at 120°C; however the cured material tends to be porous.

Certain polymer adhesives with a low percentage of volatile constituents are vacuum compatible and may be used in a vacuum environment if temperatures are kept within allowable limits. For example, Torr-seal™ epoxy cement is a low vapor pressure epoxy material capable of being used to 100°C. Where electrical conductivity is desired, copper or silver flakes can be added to the adhesive.[121]

3.8.2 Non-Permanent Joining

Often surfaces must be joined to make a vacuum-tight seal but which in the future will be disassembled. The type of joint that is made can depend on how often the joint needs to be disassembled and in some cases other factors such as thermal conductivity or electrical conductivity.

Solder is defined as a joining material that has a melting point of less than 475°C. Solder seals use vacuum-compatible low melting point

alloys of indium, tin, gallium, lead, and their alloys. The seals can "broken" by moderate heating of the joint. All of these materials have good ductility and can be used where the joint may be stressed due to differences in the coefficient of expansion, mechanical stress, etc. Some low-melting metals that have low vapor pressures at their melting point are listed in Table 3-9.

Table 3-9. Melting Point (MP) and Vapor Pressures of Some Metals Used for Sealing

• Indium	(MP 156°C)	- vapor pressure at MP < 10^{-11} Torr
• In-3% Ag (eutectic)	(MP 147°C)	- vapor pressure at MP < 10^{-11}
• Gallium	(MP 30°C)	- vapor pressure at MP < 10^{-11}
• Tin	(MP 231°C)	- vapor pressure at MP < 10^{-11}
• Lead	(MP 327°C)	- vapor pressure at MP = 10^{-8}

Note: Indium and gallium can cause grain boundary embrittlement in aluminum.

Solder glasses have a high lead content and melt at 400–500°C. They may be used to join glasses at low temperatures. Sodium silicate ("water glass") can be used in gel form for sealing surfaces and bonding surfaces although it outgasses extensively. Silver chloride AgCl (MP 455°C) can be used as a solder seal for glass. It is an electrically insulating seal material that is insoluble in water, alcohols and acids, but can be dissolved in a water solution of sodium thiosulfate.[122]

Solid metal seals can be formed by deformation of a soft metal on a hard metal surface. The deformation may be by compression of soft metals such as aluminum or gold between hard surfaces, or by shear of a soft metal, such as annealed copper, by a knife-edge (Conflat™ or CF flange[123]) Typically flanges with these seals are held together with bolts and the torquing sequence is important, particularly on large flanges. This type of seal is used with UHV vacuum systems and may be heated to 400°C. Higher temperatures anneal the stainless steel so that the knife-edge does not shear well.

Elastomer seals such as "O" rings should be designed with a specific compression of typically 30–40 %. "O" rings are molded so there is a parting line on the "O" ring where the mold-halves meet. This parting line should be along the axis where the sealing surfaces meet—the "O"

ring should never be twisted such that the parting line is across a sealing surface. Critical sealing material should be radiographed in order to assure that the seals contain no inclusions that might cut the sealing material during deformation (*MIL-STD 00453*). Surfaces contacting the seal material should be smooth with a 32 microinches RMS finish or better, and contain no scratches. The sealing surfaces can be textured in the axis of the sealing ring—this is often done by hand with emery paper. The flange surfaces should be flat and parallel so that as the surfaces are pulled together the elastomer is compressed uniformly. There should be some play in the flanges to allow them to align parallel without stress. This may necessitate a flexible section, such as a bellows, in the plumbing.

Gases permeate polymer seal materials but the polymer seals have the advantage of being reusable. Black "O" rings are loaded with carbon. Sliding or decomposition can release particulates from the rubber. Seal material can be obtained without the carbon loading. Buna-N rubber may be used for sealing to 10^{-5} Torr and 80°C, but pure Viton™ can be used to 10^{-6}–10^{-8} Torr and to 200°C. When using Viton™ it is important to specify pure 100% Viton™ as the term Viton™ can be used for polymer blends. Teflon™[124] is a poor sealing material since it takes a "set" with time and looses its compression, but it can be used with a "canted-coil" spring arrangement such as used with metal O-rings.

Elastomer seals perform poorly at low temperatures since they lose their elasticity as the temperature is reduced. If elastomer seals are to be used on systems that are to be cooled, the elastomer seal area should be heated. Excessive heat degrades the seal material. If the seal area is heated during processing, the seal area should be cooled. Elastomers should be very lightly lubricated with a low vapor pressure grease to allow sliding and sealing. Elastomers should be cleaned and re-greased periodically. Cleaning may be done by wiping with isopropanol (not acetone) using a lint-free cloth. Elastomer seal material can be glued to itself using cyanoacrylate ester glue ("superglue") or a commercial vulcanizing kit. Place the glued joint in a non-bent region of the O-ring groove if possible. Elastomer seals can be formed by vulcanization of the elastomer directly on metal surfaces. Inflatable elastomer seals (Pneuma-Seal™) are available for sealing large areas or uneven surfaces. These seals can sometimes be used with warped flanges.

A resilient (elastic) metal "C" ring gasket that uses a "canted-spring-coil" inside a metal "C" ring can be used like an elastomer "O" ring and is very useful in applications where frequent demounting is important, but elastomer materials are not appropriate. This seal can be obtained with

different metal sealing surfaces made by plating the outer steel surface with gold, silver (typical) or indium.

3.8.3 Lubricants for Vacuum Application

Liquid lubricants can be used in vacuum systems.[125] Their primary problems are containment at the desired location due to surface creep, and vaporization. Silicone diffusion pump oil with suspended graphite particles has been used to lubricate Viton "O" rings and has been found to decrease pressure bursts from the O-rings when they are used for motion in a UHV environment.[126] Many fluid lubricants will form an insulating layer when exposed to a plasma thus giving rise to electric charge buildup and arcing in the plasma system. Some properties of lubricant fluids suitable for vacuum use are given in Table 3-10.

Table 3-10. Vapor Pressures of Some Vacuum Greases

Material	Vapor pressure at room temp (Torr)
silicone	10^{-8} to 10^{-9}
fluorocarbon	10^{-10} to 10^{-12}
polyfunctional ester	10^{-10}
polyalphaolephin	10^{-10}
polyphenylether	10^{-12}
Apiezon™ Type L grease	8×10^{-11}
Apiezon™ Type M grease	2×10^{-9}

There are several low vapor pressure solid (dry) lubricant and anti-stick (anti-seize) compound materials that are vacuum compatible. These include the sulfides (MoS_2 and WS_2—lubricants, usable to 10^{-9} Torr), silicides (WSi_2—anti-stick) and the selenides (WSe_2—electrical conductors,). Care should be taken to insure that any binder materials used in the materials are also vacuum compatible. Sputter deposited MoS_2 and MoS_2 +Ni lubricants, in particular, have been shown to be acceptable in vacuum and are used by NASA for space applications.[127]-[131] Burnishing is another way of applying solid lubricants. Solid lubricants can be

incorporated into a surface to give a lubricating action. For example, PTFE can be incorporated into electrodeposited nickel and then act as a lubricant for the nickel surface.[132] The primary problems with solid lubricants are: wear, particulate generation, moisture sensitivity, and production complexity.

3.9 EVALUATING VACUUM SYSTEM PERFORMANCE

The best time to characterize a processing system is when it is performing well and producing an acceptable and reproducible product. A log of the system performance during processing should be kept. Special characterization runs should be made if deemed necessary. Characteristics of a vacuum system include:

- Time to reach the cross-over pressure, i.e., from roughing to high vacuum pumping
- Time to reach a given pressure (base pressure)
- Pressure after a long pumpdown (ultimate pressure)
- Leak-up rate between given pressure levels with the pumping system valved-off
- Pressure rise during processing
- Mass spectrometer reading of gases after pumpdown and during processing
- Helium leak check of the system by bagging (i.e., bag check).

In critical applications the system performance can be evaluated by statistical analysis.[133]

3.9.1 System Records

An operations log should be kept of each system. This log should show:

- Date and time on and off, i.e., “run time”
- Pumping behavior, i.e., time to base pressure, leak-up rate, pressure rise during processing

- Mass spectrometer peak height of critical or indicative gases such as water, nitrogen, oxygen at base pressure and during processing
- Comments by the operator on system performance, i.e., does the system behave the way it has in the past?

A calibration log should be kept for components such as vacuum pressure gauging. A systematic calibration schedule may be desirable.

Are there changes in the product (film) that might be due to changes in the vacuum environment? The operator's evaluation of the film color, reflectance, and uniformity over the fixture can be noted on the process travelers. A log of work (work log) performed on the processing system such as maintenance, cleaning, modification, replacement, etc, including the date and personnel involved, should be kept. These records should be reviewed frequently and discussed with the maintenance/operator personnel.

3.10 PURCHASING A VACUUM SYSTEM FOR PVD PROCESSING

Most vacuum deposition systems are purchased from commercial suppliers. Before specifying a system and associated fixturing, make sure the processing requirements are well defined such as:

- Size and weight of the fixturing
- Feedthroughs—mechanical, electrical, component, etc.
- Processing gases to be used (if any)
- Processing parameters to be used such as temperature and time
- Gas and vapor load imposed by fixturing and full load of substrates during pump-down
- Gas and vapor load imposed by fixturing and full load of substrates during processing
- Cycle-time required (pumpdown—process—letup)

The design of a good vacuum system is not necessarily the same as the design of a good production vacuum deposition system. Generally there are trade-offs between the best vacuum design practices and practical

production requirements such as accessibility for fixture installation and system maintenance. The type of processing can define the system design.

The generic mechanics for writing Request For Quotes (RFQs) and in writing Purchase Orders (POs) for vacuum systems are discussed by O'Hanlon.[134] Initial performance tests of a system should be made at the supplier location both with the system "empty" and with typical production fixturing and substrates in place. The system should be helium leak checked with particular attention to internal water lines (pressurize the water lines with helium) and feedthroughs. Final acceptance tests should be performed at the user location after the supplier has completed installation.

Some common mistakes in system design and specification of vacuum systems are:

- The vacuum system is specified before the fixturing is detailed and fixturing requirements are known.
- Poor design of fixturing, associated feedthoughs, and process monitoring systems—this often means that the system must be modified after acceptance.
- Excess volume and surface areas in processing chamber.
- Inadequate pumping capability in all regions of the chamber when fixturing and substrates are installed producing a "crowded" chamber. This is a particularly important problem if there are high water vapor loads to be pumped. The problem of pumping water vapor in a crowded chamber may be alleviated using cryopanels.
- Inadequate pumping capability to handle gases and vapors released during processing.
- Inadequate cycle time for required production throughput.
- No vibration specifications on the processing chamber.
- Inadequate number, size and location of feedthrough and access ports into the system—be sure to allow for potential requirements.
- Inadequate accessibility for installing fixtures and for maintenance.
- No liners or shields in the system to reduce non-removable vacuum surface contamination.

- Design is not tolerant of processing or maintenance mistakes or errors—for example, molten evaporant material, particulates or maintenance tools can drop into the pumping stack in "base-pumped" chambers.
- Inadequate interlocking to protect the system from power or water failure or from operator error.
- Inadequate ballasting of the pumping manifold to reduce contamination by compression liquefaction.
- Inadequate interlocking to protect operator from high voltages.
- Improper gauge selection and improper gauge positioning.
- Inadequate specifications of construction materials and surface finishes.
- Space requirements not defined—floor "footprint," height, power, and water availability.
- System not built to accepted standards and recommended practices, e.g. ASME boiler code.
- System not thoroughly helium leak checked after assembly.
- No capability to heat system surfaces while system is open to the ambient to minimize water vapor adsorption.
- System exhaust does not meet environmental requirements and does not maintain a clean ambient in the vicinity of the system.
- Safety aspects such as belt guards, protection of glass ionization gauges, etc. have not been adequately addressed.
- No agreement on who is responsible for installation of the equipment at the user's site.
- Payment schedule that allows final payment before final acceptance.
- No spare components ("operational spares") or spare components list.
- Inadequate operating instructions and system diagrams.

- Inadequate "troubleshooting," maintenance and repair instructions.
- No warranty period on system performance.

If the operation of the equipment is unfamiliar to the user, training should be included in the purchase price since many of the equipment suppliers have training organizations. Many suppliers can furnish maintenance and repair services on call or on contract.

3.11 CLEANING OF VACUUM SURFACES

The interior non-removable surfaces of the vacuum system should be protected as much as possible from deposits from the deposition process. Removable liners and shields should be used wherever possible.

3.11.1 Stripping

Stripping is the term given to the removal of large amounts of materials from a surface, usually by chemical or mechanical means. Stripping of deposited material from surfaces such as that of the fixtures is necessary when the deposit buildup interferes with the processing or the yield. For example, film buildup of a brittle, highly-stressed material can create flaking that produces particulate contamination in the deposition system. In some cases, the time between stripping of surfaces can be increased by overcoating the deposited material with a ductile material such as aluminum. Overcoating can also be useful when stripping toxic materials such as beryllium from surfaces.

The most simple stripping technique is to apply an adhesive tape and pull the deposit buildup from the surface. In the semiconductor industry they use blue "dicing tape" for this procedure. Tape-stripping can be assisted by having a release agent on the surface. Common release agents are carbon[135] and boron nitride (e.g. Combat™) applied to the vacuum surface in a water slurry. Carbon release agents can also be applied by glow discharge decomposition of a hydrocarbon vapor.[136][137] The oxide on the surface of stainless steel acts as a natural release agent for films of deposited materials such as copper or gold that do not adhere well to oxides. A deposited metallic film can be used as a release agent. For

example, an aluminum film can be dissolved by a sodium hydroxide solution and a molybdenum film can be dissolved by a hydrogen peroxide solution.

Deposit buildups can also be removed by abrasion, with grit blasting and dry or wet glass bead blasting[138]-[140] being common techniques. A common kitchen scouring pad such a Scotchbrite™ is a good abrasive pad. Dry glass bead blasting is a commonly used cleaning technique but, as with other grit abrasive techniques, can leave chards of glass embedded in soft surfaces. The amount of grit embedded depends on how long the glass beads have been used, i.e. how much they have been fractured. Water soluble particles can be used for abrasive cleaning and allow easy removal of the water-soluble embedded particles. For example, 5 micron sodium bicarbonate (baking soda) particles entrained in a high velocity water stream can be used for mild abrasive cleaning. The bead blasting can also deform the surface and trap oil contamination if the surface is not clean before bead blasting. Polymer beads can be used in some cases.[141]

Grit blasting uses grit such as fractured cast iron, alumina, silica, plastic, etc. of varying sizes and shapes accelerated in a gas stream to deform and gouge the surface.[142] Particles can be entrained in a high velocity gas stream by using a siphon system or a pressure system such as used in sand blasting equipment. In addition to removing gross contamination, grit blasting roughens the surface. The Society of Automotive Engineers (SAE) has developed specifications on grit size (Table 2-3). Bombardment of a surface by grit is like "shot peening" and places the surface in compressive stress which can produce unacceptable distortion of thin materials.

In some cases, the surfaces of fixtures are deliberately roughened so as to prevent the easy removal of deposit buildup since flaking of deposited material can be a source of particulates in the vacuum system. Roughening is typically done using grit blasting.

Chemical etching can often be used to remove the deposit buildup[143]-[146] without attacking the underlying material. Table 3-11 lists a number of etchant solutions that can be used to remove the material indicated. Also listed are some plasmas that can be used to remove the material indicated. Chemical etching is also used to remove films from coated parts to "rework" the parts.

3.11.2 Cleaning

Cleaning, handling, and storage of vacuum surfaces should be done with as much care as the preparation of substrate surfaces discussed

in Ch. 12. When cleaning vacuum system surfaces, care should be taken to not increase the surface area any more than necessary. Often simple cleaning processes work better than more elaborate processes.[147][148] Metal surfaces can often be cleaned by:

- Detergent wash
- Rinse in 50:50 DI water and ethanol
- Rinse or wipe with anhydrous ethanol or acetone

A simple wipedown of a metal is as follows:[149]

- Neutral pH solvent (perchloroethane or trichloroethane)
- Acetone
- Anhydrous methanol or ethanol

Note: Acetone tends to leave a residue. Acetone cleaning should be followed by a methanol or ethanol rinse.

Aluminum surfaces should be cleaned with care since the oxide formed on the aluminum is very fragile and can easily be degraded by improper handling and cleaning. The chloride ion is especially detrimental to aluminum oxide. Care and cleaning of aluminum surfaces should be carefully specified and controlled.

3.11.3 *In Situ* "Conditioning" of Vacuum Surfaces

The objective of surface conditioning is to remove contaminants from the vacuum surfaces prior to the processing operation. These species are predominantly water vapor and hydrocarbon vapors to which the surfaces are exposed on being opened to the ambient environment.[150] Before the system is sealed, the vacuum surfaces should cleaned with a wipedown (Sec. 3.11.2). The most common *in situ* cleaning procedure used in PVD processing is plasma cleaning with a reactive gas such as oxygen or hydrogen* to produce volatile reaction products, e.g. hydrocarbons to CO and CO_2 (Sec. 12.11).[30][151]-[157]

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*In the TOKAMAK fusion program, at Princeton Plasma Physics Laboratory, the plasma chamber is conditioned using a hydrogen plasma and monitored by observing the hydrocarbon peaks using an RGA. In one case it was found that the system just would not clean up like it should. Finally the system was considered clean and the experiments performed. When the system was opened the imprint (residue) of a polyethyelene glove was found in the bottom of the chamber. The hydrogen plasma cleaning completely volatilized the glove.

Table 3-11. Wet Chemical and Plasma Etchants for Stripping

Material to be removed	Etchant	Ratio (vol)	Useful on these surfaces	Can damage
Al	$H_3PO_4/HNO_3/H_2O$	20/2/5	stainless steel (SS), glass (G), ceramic (C)	Cu
Al	NaOH	molar	SS,G,C	Ti,Ag
	BCl_3 (plasma)			
C	H_2O_2	10–30%	SS,G,C	Cu,Fe
	KOH/H_2O	saturated/hot	G,C	
	O_2 (plasma)		SS,G,C	Ag, Cu
	H_2 (plasma)		SS,G,C	
Cr	HCl/Glycerine	1/1	SS,G,C,Cu	Fe
Cr	$KMnO_4/NaOH/H_2O$	5 gm/ 7.5 gm/ 30 ml	SS, G, C	Al
Cu	HNO_3/H_2O	1/1	SS,G,C	Fe
Au	HCl/HNO_3 (aqua regia)	3/1	G,C	SS,Cu,Fe
Fe	HCl/H_2O	1/1	SS,G,C	———
Mo	$HNO_3/H_2SO_4/H_2O$	1/1/3	SS,G,C	Cu,Fe
	H_2O_2	10-30%	SS,G,C	Cu,Fe
Ni	$HNO_3/C_2H_4O_2/C_3H_6O$	1/1/1	SS,G,C	Cu
Pd	HCl/HNO_3	3/1	G,C	SS,Cu,Fe
Ag	NH_4OH/H_2O_2-30%	1/1	SS,G,C,Cu	———
Ta	HF/HNO_3	1/1	SS	G,C,Cu
Ti	NH_4OH/H_2O_2-30%	1/2	SS,G,C,Cu	———
W	HF/HNO_3	1/1	SS	G,C,Cu
	H_2O_2	30%	SS,G,C	Cu,Fe
	$CF_4 + O_2$ (plasma)			
Si	HF/HNO_3	1/1	SS	G,C,Cu
	$CF_4 + O_2$ (plasma)			
Ti-W	H_2O_2	30%	SS,G,C,Al	
TiC	H_2O_2	30%		
TiN	H_2O_2:NH_4OH:H_2O	1/1/1	SS,G,C,Al	
	HF/H_2O	1/1	SS,Cu	G,C
	$CF_4 + O_2$ (plasma)			
NiCr	$HNO_3/HCl/H_2O$	1/1/3	SS,G,C,Cu	———
SiO_2	HF/H_2O	1/1	SS,Cu	G,C
	CF_4 (plasma)			
Cd plating	NH_4NO_3/H_2O	120gm/liter	steel,brass,Cu	
Zn plating	HCl/H_2O	120ml/liter	brass,Cu alloys	

Note: Molar solution is one gram-molecular-weight of material per liter of water

Other *in situ* conditioning techniques include:

- Flushing the system with a hot dry gas[158]
- System bakeout, preferably to >400°C, to thermally desorb water[34]
- Sputter cleaning with argon
- UV radiation from a mercury vapor lamp in chamber to photodesorb water vapor[159][160]

An example of *in situ* conditioning and system pumping performance is shown in Fig. 3-20. The figure shows the pumpdown cycle of the system shown in Fig. 3-10.[57] The system was roughed-down using a mechanical pump followed by cryosorption pumps. High vacuum pumpdown was with a cryopump. The vacuum surfaces were then sputtered by using a positive potential on the "glow bar" (Sec. 12.11.1). The system was then pumped down again. When sputter depositing a molybdenum film, the fresh molybdenum acted as a getter giving the final pumpdown pressure.

3.12 SYSTEM-RELATED CONTAMINATION

In PVD processing, contamination can cause pinholes in the deposited film, local or general loss of film adhesion, and/or local or general changes in film properties. In many cases the deposition system is the first to be blamed for the problem. This may not be the case and other factors should always be considered.

3.12.1 Particulate Contamination

Particulates in a deposition system are generated during use from a variety of sources including:

- General and pinhole flaking of deposited film material on walls and fixtures
- Wear debris from surfaces in contact, i.e. opening and closing valves[161]
- Debris from maintenance and installation, i.e. insertion of bolts, wear of handtools, motor tools, and from personnel and their clothing
- Unfiltered gas lines

- Particulates "brought-in" with fixtures and substrates
- Particulates brought in with processing gases and vapors
- Particulates formed by gas phase nucleation of vaporized material (Sec. 5.12) or decomposed chemical vapor precursors (Sec. 4.7.4).

Film buildup on walls and fixtures may flake as it becomes thick, particularly if the film material has a high residual stress. For example, sputtering $TaSi_2$ produces a large number of particulates because the deposited material is brittle and is generally highly stressed. One way to alleviate the problem somewhat is to occasionally overcoat the brittle deposit with a softer material such as aluminum. Pinholes form in films on surfaces producing flakes and this source of particulates is called "pinhole flaking." Liners which may be easily removed and cleaned or discarded to prevent deposit buildup should be used. Heating or mechanical vibration of surfaces contributes to flaking and wear.[162]

Vibration can increase the generation of particulates. Vibration can be minimized by using pneumatic isolators.*[163] In some deposition systems, the vibration level should be specified to minimize particulate generation. For example:[164]

- For frequencies <100 Hz, velocity should not exceed 0.076 cm/s (0.030 in/s)
- For frequencies > 100 Hz, acceleration should not exceed 0.050G

Note: G is a unit of acceleration equal to the standard acceleration due to gravity or 9.80665 meters per second per second.

The control of particulate contamination in a system is very dependent on the system design, fixturing, ability to clean the system, and the gas source/distribution system.[165]-[167] The use of dry lubricants decreases wear and particle generation. In particular, bolts used in the vacuum chamber should be silver plated to prevent wear and galling. Some types of plasma etching processes generate large amounts of particulates.[168]

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*A PVD process used sublimation of chromium from particles in an open boat. The particles were heated by contact with the surface of the hot boat. Problems were encountered with process reproducibility. When asked about vibration in the system the answer was "sometimes the chromium particles even bounce out of the boat". No wonder they had a reproducibility problem!

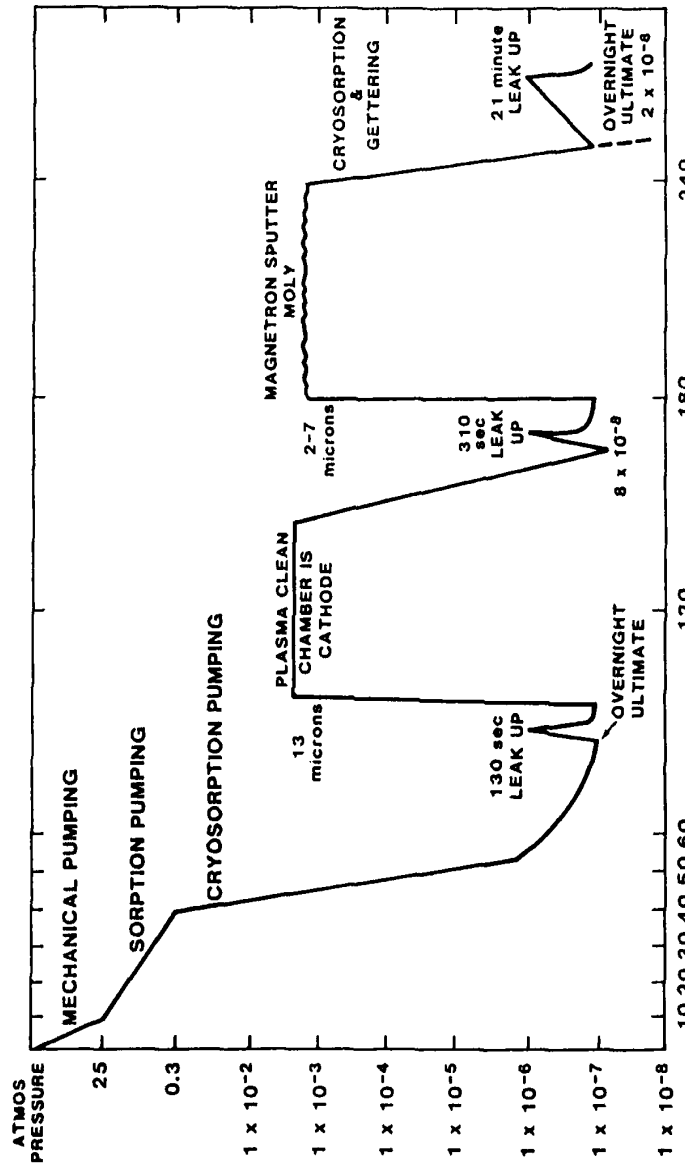


Figure 3-20. Pumpdown curve of system shown in Fig. 3-10.

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3.12.2 Vapor Contamination

Hydrocarbon vapors in the deposition chamber can originate from the vacuum pumping system. Pump oil and lubricant vapors can backstream into the system. Backfill gases can contain oil vapors from the ambient environment.

Water Vapor

The most common vapor in a good vacuum system is water vapor.[169] The water molecule is highly polar and is strongly adsorbed on clean metal and oxide surfaces. Water vapor in the vacuum system can be measured using a quartz crystal moisture sensor or Surface Acoustic Wave (SAW) sensor[170] which adsorbs water and changes properties. Water vapor often presents a major variable in many PVD processes. Water and water vapor in the vacuum system affects the pumpdown time and the contamination level during the deposition process. Water vapor is much more difficult to pump-away than is a gas because the water vapor molecule has a long "residence time" on a surface compared to the gas molecule (Table 3-5). Thus if many adsorption-desorption collisions are necessary for the water molecules to be removed, the time to reduce the chamber pressure to a given basepressure will be long compared to an "open" system.

Water will adsorb to many monolayer thickness of the surfaces and each monolayer will be progressively harder to remove from the surface by thermal vaporization. Figure 3-5 shows some partial pressures of water vapor, as a function of pumping time, that might be expected in a system if you start with wet surfaces and dry surfaces. Note the time scale is in hours. If there is a quantity of liquid water in the system the evaporation rate may freeze the water into ice. This lowers its vapor pressure which decreases the ability of the pumps to remove water from the system.

The best procedure for eliminating water vapor in the vacuum chamber is to prevent its introduction in the first place. This can be done by: (1) backfilling with a dry gas, (2) reducing the time the system is open to the ambient, (3) maintaining a flow of dry gas through the system while it is open, (4) keeping the chamber walls and surfaces warm to prevent condensation, and (5) drying and warming the fixtures and substrates before they are introduced into the chamber. Large volumes of dry gas can be obtained from the vaporization of liquid nitrogen (LN2) usually from above the LN2 in a tank (1 liter of LN2 produces 650 liters [stp] of dry gas),

by compression and expansion of air or by using high volume air dryers. Gas dryers dry gas by desiccants, refrigeration or membrane filtering.

When introducing substrate materials that can absorb moisture, such as many polymers, the history of the material may be an important variable in the amount of water vapor released by outgassing in the deposition chamber. In this case the history of the material must be controlled and perhaps the materials outgassed before they are introduced into the deposition chamber. In some web coaters, the web material is unwound in a separately pumped vacuum chamber before it is introduced into the deposition chamber. This isolates the deposition chamber from most of the water vapor released during the unrolling operation.

3.12.3 Gaseous Contamination

Contamination from the processing gas can come from an impure gas source or contamination from the distribution line. Distribution lines for gases should be of stainless steel or a fluoropolymer to reduce contamination. Gases can be purified near the point-of-use using cold traps to remove water vapor or purifiers to remove reactive gases. Purifiers may be hot metal chips or cold catalytic nickel surfaces and should be sized to match flow requirements. Reactive gases can come from the ambient processing environment around the system.

3.12.4 Changes with Use

The contamination in a system will change with use due to changes in the surface areas, buildup of contaminants that are not removed, and changes in materials properties such as degradation of pump oils. Proper records noting product yield will allow establishing an appropriate periodic cleaning and maintenance program.

3.13 PROCESS-RELATED CONTAMINATION

Often the process introduces contamination into the deposition system. This contamination can be associated with removeable surfaces such as fixtures, with the source material, with the substrate material, or with processes related to the deposition process itself such as ultrafine particles

from vapor phase nucleation of the vaporized source materials. These sources of contamination are discussed in the chapters related to the PVD process involved.

Surfaces and materials that are to be introduced into the deposition system should be cleaned and handled commensurate with the contamination level that can be tolerated (Ch. 12).

3.14 TREATMENT OF SPECIFIC MATERIALS

3.14.1 Stainless Steel

The natural oxide on stainless steel can be removed by:[171]

- Vapor clean in trichloroethane for 5 minutes
- Rinse in cold water
- Hot alkaline cleaner for 5 minutes
- Rinse in hot water
- Potassium permanganate (100 ml DI water + 50 g NaOH + 5 g $KMnO_4$ at 95°C)—soak to condition oxide scale
- Hydrochloric acid dip to sensitize surface (remove natural oxide passivation)
- Pickle (30 vol% HNO_3 + 3 vol % HF) at room temperature for 30 minutes
- Rinse in hot deionized water

Stainless steel can be chemically polished by:[171]

- Clean in a hot alkaline solution
- Rinse
- Activate in a hot 5% sulfuric acid solution for 5 minutes before polishing.
- Chemically polish at 75°C in a solution of:

  nitric acid—4 parts

  hydrochloric acid—1 part

  phosphoric acid—1 part

  acetic acid—5 parts

Stainless steel can be electropolished (anode) by:

#1	H_2SO_4 (1.84 specific gravity)	1000 ml
	H_2O	370 ml
	Glycerin (USP)	1370 ml
	Add acid slowly to water (to avoid overheating) then add glycerin	
	Use carbon or lead cathode	
	Polish at 7.5 volts for about 30 sec	
	Rinse in deionized water	

#2	Phosphoric acid	75 to 100%
	Water	25 to 0%
	Current density, amps/ft^2	300
	Temperature	70°C

#3	Phosphoric Acid	5 parts
	Sulfuric acid	4 parts
	Glycerin (USP)	1 part
	Current density, amps/ft^2	450

3.14.2 Aluminum Alloys

The natural oxide on aluminum can be removed (stripped) before polishing. A chemical strip for the oxide on aluminum is:

- Soak in solution of 5% NaOH by weight at 70–75°C
- Soak in a solution of 1 part concentrated HNO_3 to 1 part deionized water at 20°C, followed by a dip in a solution of 1 part concentrated HNO_3 with 64 g/liter NH_4HF_2 at 20°C (desmutting procedure)
- Rinse well.

Aluminum alloys can be chemically polished by:

#1	Dip into 10% HCl
	Rinse in deionized water

#2 Solution[155]

H_3PO_4—80%

CH_3COOH—15%

HNO_3—5%

Temperature

90–110°C

Dip for 2–4 min

In etching 6061-T6 aluminum alloys for barrier anodization the following cleaning/polishing procedure has been used:[118][172]

- 5% NaOH by weight at 70–75°C for 5 min
- 1 part concentrated HNO_3 to 1 part H_2O by volume at 20°C for 10 min
- Concentrated HNO_3 with 64 g/l NH_4HF_2 at 20°C for 10 min (desmutting)
- Rinse in deionized water
- Use within 30 minutes

Aluminum alloys can be electropolished (anode) by:

Cathode of stainless steel, lead or carbon

#1	Sodium carbonate	15% (wt)
	Trisodium phosphate (TSP)	5% (wt)
	Water solution	
	Current density, amps/ft^2	50–60 at start
	Temperature	75–80°C
#2	Fluoroboric Acid (con)	2.5% (vol)
	Water solution	
	Current density, amps/ft^2	10–20
	Voltage	15–30
	Temperature	30°C

#3	Sulfuric acid (con)	1 to 60% (vol)
	Hydrofluoric acid (con)	0.2 to 1.5% (vol)
	Water	
	Current density, amps/ft^2	100
	Temperature	60°C

# 4	Perchloric acid (con)	35% (vol)
	Acetic anhydride (con)	65% (vol)
	Current density, amps/ft^2	10
	Temperature	15°C

An aluminum surface can be smoothed ("brightened") by dipping in 10% HCl followed by a thorough rinse in deionized water. Aluminum surfaces can be roughened and their chemical composition altered to allow better adhesion when the surface is adhesively bonded.[173]

Heavily corroded aluminum alloys can be electrocleaned by:

- Pickling in 5% NaOH solution at 75°C
- Wash in 30% HNO_3
- Dip in 12% H_2SO_4 followed by
- An anodic electroetch at 90°C in a solution of 100 g H_3BO_3 and 0.5 g borax in 1 liter deionized water starting at 50 volts and increasing to 600 volts

3.14.3 Copper

The oxide on copper can be stripped by:

#1 Clean in perchloroethylene

Ultrasonic clean in alkaline detergent (pH = 9.7) at 60°C for 5–10 minutes

Rinse

Deoxidize in 50 vol % HCl at room temperature for 5–10 minutes

Rinse

#2 Solvent clean

Immerse in solution of 60 ml phosphoric acid (specific gravity 1.75), 10 ml nitric acid (specific gravity 1.42), 10 ml acetic anhydride and 8 ml water for 4 min at room temperature.

Rinse

Copper can be chemically polished. Copper can be polished (smoothed) by:

- Immerse in solution of

  60 ml phosphoric acid (specific gravity 1.75)

  10 ml nitric acid (specific gravity 1.42)

  10 ml acetic anhydride and

  8 ml water

  for 4 minutes at room temperature.

Copper can be electropolished by:

#1 Becco process

Sulfuric acid	14% (wt)
Phosphoric acid	49% (wt)
Chromic acid	0.5% (wt)
Water	36.5% (wt)
Current density, amps/ft^2	100 to 1000
Temperature	20 to 70°C

3.15 SAFETY ASPECTS OF VACUUM TECHNOLOGY

Vacuum technology presents some unique safety hazards in addition to the usual mechanical and electrical hazards.[174] Some points to remember are:

- Hazardous gases can accumulate in pump oils and cryosorption pumps. This can lead to problems during maintenance and disposal.
- Pumping pure oxygen using hydrocarbon pump oils in mechanical pumps can lead to an explosion (diesel effect).

- Floating surfaces in contact with a plasma can attain a high electrical potential if the plasma is in contact with a high potential at some other point in the system. Surfaces that can be touched by personnel should be grounded.

3.16 SUMMARY

In order to have a reproducible PVD process it is important to have a good vacuum environment. Contamination can originate in the deposition system itself and it is important that this source of contamination be considered as well as contamination from the external processing environment and from the as-received material.

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4

The Low-Pressure Plasma Processing Environment

4.1 INTRODUCTION

A plasma is a gaseous environment that contains enough ions and electrons to be a good electrical conductor. Plasma processing is a general term for processes using a plasma environment where the plasma is an essential part of the processing. Often in a PVD processing plasma, the degree of ionization is low (i.e., a weakly ionized plasma) such that there are many more gaseous neutrals than there are ions. Generally in PVD deposition processes, plasmas are used:[1]

- As a source for inert (Ar^+, Kr^+, Hg^+) and/or reactive (O^+, N_2^+) ions that can be accelerated to high energies
- As a source of electrons
- As a means for cleaning surfaces by "ion scrubbing," physical sputtering, or plasma etching
- For creating new chemical species by plasma chemistry effects such as Si_2H_6 from SiH_4 or O_3 from O_2, etc.
- As a means of "activating" reactive species by forming excited species, radicals, and ions and adding thermal energy by collision processes
- As a source of ultraviolet radiation

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Plasmas are typically established in low pressure gases though they may be found in atmospheric ambient or higher pressures, where they can be in the form of a corona discharge[2] or an arc discharge.[3]

In order to have a good plasma system for PVD processing the system should first be a good vacuum system (Ch. 3). One major difference between a system used for vacuum processing and one used for plasma processing is that often the conductance of the pumping system in the plasma system is reduced to minimize the flow of processing gases through the system. This reduced conductance reduces the ability of the system to "pump-away" system-related contaminants and process-related contaminates generated during the processing. In addition many contaminants are "activated" in the plasma making them more chemically reactive. Thus contamination is often more of a concern in a plasma system than in a vacuum system. Another concern in a plasma system is plasma uniformity which depends on how the plasma is generated and the geometry of the system, the electrodes and the fixturing.

If a high DC voltage is applied between two electrodes in a vacuum, the electrical response will depend on the gas pressure. At a very low pressure only the naturally occurring ions, formed by natural radiation, will be collected. As the gas pressure increases, ions and electrons will be accelerated, ions will be generated by electron-atom collisions and the current will increase. At higher pressures, a normal glow discharge will form a bright spot (cathode spot) on the cathode. Most of the potential drop will occur near the cathode. As the pressure increases further, the cathode spot will maintain the same current density but will grow in size. When the spot covers the cathode, the cathode current density will be a function of the gas pressure and this region is called the abnormal glow discharge region. A plasma will fill the region between the electrodes even though most of the potential drop will be near the cathode across the cathode fall region. As the pressure increases, the plasma between the electrode acts as a better and better electrical conductor until finally an arc is formed and the voltage between the electrodes will fall and the current density will increase.

4.2 THE PLASMA

A weakly ionized plasma is one that has only a small portion of the gaseous species ionized with the rest being neutrals some of which may be "excited." An "equilibrium plasma" is one that is volumetrically charge-neutral having an equal numbers of ions and electrons per unit volume. Plasmas are maintained by the continuous introduction of energy which accelerates electrons to energies which are capable of ionizing atoms by electron-atom collisions.[4][5] The inelastic collisions between electrons and atoms/molecules in the plasma produce a large number and variety of excited species, radicals, and ions without having to have a high thermal gas temperature, as is necessary in thermal (flame) ionization.

4.2.1 Plasma Chemistry

The plasma is an energetic environment in which a number of chemical processes can occur. Many of these chemical processes occur because of electron-atom collisions.

In a sustained plasma, electrons are accelerated in an electric field. The sources of electrons are from:

- Secondary electrons from an ion or electron bombarded surface
- Ionizing collisions where an atom loses an electron
- Electrons from a hot thermoelectron emitting source (hot cathode)

When heated, some surfaces emit copious amounts of electrons (thermoelectron emission). Tungsten and thoriated tungsten are common examples but lanthanium hexaboride (LaB_6) is an interesting material in that at a temperature of 1700°C, it has an electron emission of >20A/cm^2[6] which is much higher than that of tungsten at the same temperature. Hot surfaces of these materials are used as electron sources in some ion and plasma sources.

Excitation

Excitation is the elevation of outer-shell electrons of the atom to a higher energy state (Sec. 2.3.1). Figure 2-3 shows the energy levels for

copper. Excitation may be very short-lived where the electrons return spontaneously to the ground energy state and emit optical radiation or may be stable where some collision process is necessary to de-excite the atom. These long-lived states are called metastable states. For example, $Ar + e^- \rightarrow Ar^*$ (metastable) + e^-. Table 4-1 gives the metastable excitation energies of some atoms.

Table 4-1. Ionization and Metastable Excitation Energies

First Ionization Energy			
Ar	15.7 volts	O	13.6 volts
Al	6.0	CH_4	14.1
Au	9.8	C_2H_2	11.6
Cl	12.9	C_6H_6	9.6
Cr	6.7	Cl_2	13.2
F	17.3	F_2	17.8
H	13.5	H_2	15.6
He	24.4	HCl	13.8
Hg	10.3	NO	9.5
Na	5.1	N_2O	12.9
Ne	21.4	O_2	12.5
Second Ionization Energy			
Ar	27.76	Na	47.0
O	34.93	Cr	16.6

Metastable Energy Levels (eV)		
He	19.82,	20.61
Ne	16.62,	16.71
Ar	11.55,	11.72
Kr	9.91,	9.99
Xe	8.31,	8.44

The de-excitation emission spectrum from the plasma is characteristic of the species in the plasma. For example, the emission spectra of copper is green, sodium vapor is yellow, mercury vapor is blue-green, oxygen is white, nitrogen is red, and air is pink. The emission spectrum can be used for plasma diagnostics and to monitor and control the density of species in the plasma.

Ionization by Electrons

Positive ions are formed by atoms or molecules suffering an inelastic collision with an energetic electron in which an electron is lost from the atom or molecule (electron impact ionization). The degree of ionization of the plasma depends strongly on the electron density and energy distribution in the gas.

$$Ar + e^- \rightarrow Ar^+ + 2e^-$$
$$O_2 + e^- \rightarrow O_2^+ + 2e^-$$

The maximum ionization probability (crossection) occurs when the electrons have an energy of about 100 eV. At high electron energies, the crossection for collision is low and high energy electrons can move through the gas rather easily. Figure 4-1 shows the ionization probability as a function of electron energy.

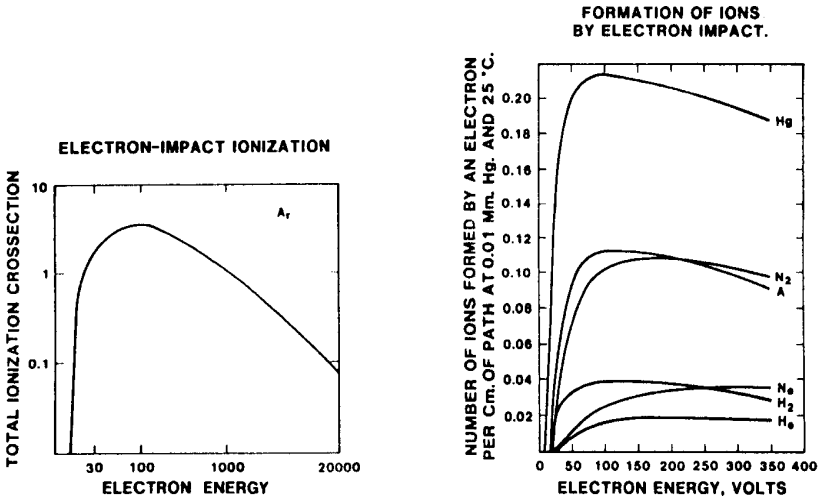


Figure 4-1. Ionization probability as a function of electron energy.

The energy necessary to remove the first electron, the second electron etc. is characteristic of the specific atoms. Table 4-1 gives the first and second ionization potentials for various atoms.

In electron attachment ionization, negative ions are formed by electron attachment in the gas. These plasmas can be very electronegative and are used in plasma anodization.

$$O_2 + e^- \rightarrow O_2^-$$

Dissociation

Dissociation is the electron impact fragmentation of molecules to form charged (radicals) or uncharged fragments of the molecule.

$$O_2 + e^- \rightarrow 2O + e^-$$
$$O_2 + e^- \rightarrow O + O^-$$
$$SF_6 + e^- \rightarrow SF_5^- + F$$
$$H_2O + e^- \rightarrow H^o + OH^-$$

Penning Ionization and Excitation

Penning ionization and Penning excitation is the ionization (or excitation) of an atom by the transfer of the excitation energy from a metastable atom whose excitation energy is greater than the ionization (or excitation) energy of the first atom. The crossection for Penning ionization is greater than for electron impact ionization so Penning ionization is an important ionization mechanism in "mixed plasmas" containing more than one species. For example, a copper atom moving through an argon plasma can be ionized by collision with metastable argon atoms.

$$Ar^* \text{ (metastable)} + Cu \rightarrow Ar + Cu^+ + e^-$$

Argon has metastable states of 11.55 and 11.75 eV and the ionization energy of copper is 7.86 eV. Thus a copper atom colliding with a metastable argon atom is easily ionized. Metastable atoms may be very effective in ionizing other species by collision. For example, a small amount of nitrogen in a neon plasma greatly facilitates maintaining the neon discharge.

Charge Exchange

Charge exchange occurs when an energetic ion passes close to a thermal neutral and there is a transfer of an electron forming an energetic neutral and a thermal ion. This process gives rise to a spectrum of energies of the ions and neutrals in a plasma.[8]-[10]

Photoionization and Excitation

In photoionization or photoexcitation processes, photon radiation is adsorbed by a molecule to the extent that ionization or excitation occurs.[11] This process is important in "laser-induced" chemical processing.

$$O_2 + h\nu \rightarrow O + O^+ + e^-$$

where $h\nu$ is the energy of a photon

An example of this process is laser-induced CVD where the radiation frequency is tuned to the vibrational frequency of the precursor molecule to enhance decomposition This resonance adsorption/excitation is the basis of laser-induced fluorescence that may be used to determine species on a surface or in the gas phase.[12][13]

Ion-Electron Recombination

Electron-ion recombination (neutralization) occurs when ions and electron combine to form a neutral species.

$$Ar^+ + e^- \rightarrow \text{surface} \rightarrow Ar^o$$

The electron-ion recombination process occurs mostly on surfaces and releases the energy taken up in the ionization process. This recombination, and the associated energy release, aids in desorption in the ion scrubbing of surfaces (Sec. 12.10.1).

Plasma Polymerization

In plasma polymerization, monomer vapors are crosslinked to form a polymer either in the plasma or on a surface in contact with the plasma.[14][15] The process can occur with either organic and inorganic monomers. Examples are the formation of amorphous silicon (a-Si:H) from SiH_4 and hydrocarbon polymer films from gaseous hydrocarbon species.

Unique Species

Species in the plasma can combine to give unique species which can have special properties such as high adsorption probabilities.[7]

$2SiH_4 \rightarrow \text{plasma} \rightarrow Si_2H_6 + H_2$
$O_2 \rightarrow \text{plasma} \rightarrow O + O_2 \rightarrow O_3$

Plasma "Activation"

Many of these plasma processes serve to plasma activate gases i.e., to make them more chemically active by dissociation, fragmentation, ionization, excitation, forming new species, etc. These activated gases impinge on the substrate surface or, if ionized, can be accelerated to the substrate by a substrate bias thereby enhancing "reactive deposition" and "reactive etching" processes. Generally contaminant gases and vapors, such as water vapor and O_2, in plasma-based processes are more significant than the same contaminant level in a vacuum-based deposition process because of the plasma activation.

Crossections and Threshold Energies

Many plasma processes are characterized by crossections for processes and threshold energies for chemical processes. The crossection for interactions are often far greater than the physical dimensions. For example, the crossection for $O_2 + e^- \rightarrow O_2^+ + 2e^-$ is 2.7×10^{-16} cm^2. Both the crossection and the threshold energy are important for reaction. For example, SF_6 and CF_3Cl have a high crossection and low threshold energy (2-3 eV) for electron dissociative attachment. They act as electron scavengers in a plasma. CF_4 has a low crossection and high threshold energy (5-6 eV) for electron dissociative attachment and CCl_4 is not activated by electron attachment at all. SF_6 and CF_3Cl are much more easily activated than is CCl_4 or CF_4.

Thermalization

Energetic molecules moving through a gas lose energy by collisions with the ambient gas molecules, scatter from their original direction, and become thermalized (Sec. 3.2.2).

4.2.2 Plasma Properties and Regions

Plasma properties include: total particle density, ion and electron densities, ion and electron temperatures, density of various excited species, and gas temperature. If there is a mixture of gases the partial densities and flow rates of the gases can be important. In a plasma these properties can vary from place-to-place. In general, a plasma will not sustain a pressure differential except in the region of a pumping or gas-injection port. However, local gas temperature variations can create variations in the molecular densities, particularly in the vicinity of a cathodic surface. This molecule density variation can be reflected in the deposited film properties due to differing bombarding fluxes and differing concentration of activated reactive species. This can produce problems with position equivalency. In some regions there can be a different number of electron and ions in a given volume and a space charge region is established.

Typical property ranges for weakly ionized plasmas at low pressures (10^{-3} Torr) are:

Ratio of neutrals to ions	10^7 to 10^4 : 1
Electron density	10^8 to 10^9 /cm^3
Average electron energy	1 to 10 eV
Average neutral or ion energy	0.025 to 0.035 eV (higher for lower pressures)

For a weakly ionized plasmas of molecular species the radical species can outnumber the ions but are still fewer than the number of neutrals.

Strongly ionized plasmas are ones where a high percentage of the gaseous species are ionized. In microwave plasmas and arc plasmas the ionization can almost be complete. One advantage of the microwave plasma is that even though the ionization is high, the particle temperatures are low.

High enthalpy plasmas are those that have a high energy content per unit volume and are sometimes called thermal plasmas. Thermal plasmas have a high particle density, are strongly ionized and are of gases that have high ionization energies. This type of plasma is used in plasma spray processes.

In plasma discharges it has been shown that the gas flow is affected by the electric fields and associated ion motion (discharge pumping).[16]-[18] This gas flow can entrain molecules injected into the plasma region and give preferential mass flow. Plasmas may be easily steered by

moving the electrons in a weak magnetic field with the ions following the electrons in order to retain volumetric charge neutrality.

Plasma Generation Region

In the plasma generation region, electrons and ions are accelerated in an electric field. At low pressures, these particles can attain high kinetic energies and may damage surfaces placed in that region.

Afterglow or "Downstream" Plasma Region

As one moves away from the plasma generation region the plasma temperature decreases, ions and electrons are lost due to recombination and the number of energetic electrons is diminished. This region is called the plasma afterglow region, and in deposition and etching processes, this position is called the "remote" or "downstream" location.[19] Other gases or vapors can be introduced into this region to "activate" them by collision with the metastable species. Substrates placed in this location are not exposed to the energetic bombardment conditions found in the plasma generation region.

Measuring Plasma Parameters

There are many techniques used to characterize a plasma.[20] Analysis of the optical emission from de-excitation is probably the most common technique used to analyze and control plasmas.[21] For example, optical emission spectroscopy is used to monitor the plasma etching process by monitoring the presence of the reactive species that are consumed or more often, the reactant species formed by the reactions. The magnitude and shape as a function of time of the emission curve, can give an indication of the etch rate and the etching uniformity. The completion of the etching process is detected by the decrease of the emission of the reactant species (endpoint analysis).[22] Actinometry compares the emission interactions of the excited states of reference and subject species to obtain the relative concentrations of the ground states.[23] Doppler broadening of the emission lines can be used to indicate temperatures and method of excitation. Optical emission characteristics are used both for process monitoring and for process control.[24]

Laser induced fluorescence spectroscopy is used to investigate plasma-surface interactions[12] and for impurity diagnostics in plasmas.[25] Optical adsorption spectroscopy can also be used to characterize the gaseous and vapor species and temperature in a gas discharge.[26][27]

Large area electrodes determine the plasma potential in the nearby volume. Small area probes, such as Langmuir probes, do not significantly affect the plasma and the electron and ion densities in a plasma can be measured by these probes.[20][28] A small insertable-retractable probe is commercially available which profiles the plasma along its track.

The electron density in the path of a microwave adsorbs energy and attenuates the transmitted signal. This microwave attenuation can be used to analyze the plasma density.[20] A plasma has an effective index of refraction for microwave radiation. By measuring the phase shift of transmitted/received microwave radiation as it passes through the plasma, the charge density can be determined. Generally the phase shift is determined by interferometric techniques.

4.3 PLASMA-SURFACE INTERACTIONS

Electrons and ions are lost from the plasma to surfaces—there is relatively little recombination in the plasma volume. Under equilibrium conditions an equal number of ionized molecules are generated as are lost from the plasma. When surfaces, electrodes, or electric fields are present, the plasma may not be volumetrically neutral in their vicinity.

4.3.1 Sheath Potentials and Self-Bias

The plasma sheath is the volume near a surface which is affected by loss of plasma species to the surface.[29] Electrons have a higher mobility than ions so electrons are lost to the surface at a higher rate than are the ions, this produces a potential (sheath potential) between the surface and the plasma. If the surface is grounded, the plasma is positive with respect to ground. If the surface is electrically floating and the plasma is in contact with a large-area grounded surface, the floating surface will be negative with respect to ground. The sheath potential is dependent on the electron energy, the electron flux, and the area of the surface. The sheath potential can vary from a few volts in a weakly ionized DC diode discharge to

50–75 volts when energetic electrons impinge on the surface at a high rate. The sheath potential is the negative self-bias that accelerates positive ions from the plasma to the surface, producing "ion scrubbing" of the surface at low potentials and physical sputtering of the surface at higher potentials.[30] This physical sputtering can be a source of contamination from surfaces in a plasma system.

It is possible for a surface in contact with a plasma to generate a positive self-bias. This occurs when electrons are kept from the surface by a magnetic field but positive ions reach the surface by diffusion. An example is in the post cathode magnetron sputtering configuration with a floating substrate fixture which can attain a positive self-bias.

4.3.2 Applied Bias Potentials

Because the electrons have a very high mobility compared to positive ions, it is impossible to generate a high positive bias on a surface in contact with a plasma. The negative potential between the plasma and a surface can be increased by applying an externally generated negative potential to the surface. This applied potential can be in the form of a continuous Direct Current (DC), pulsed DC, alternating current (AC) or radio-frequency (rf) potential. This applied bias can accelerate positive ions to the surface with very high energies.

4.3.3 Particle Bombardment Effects

Energetic ion bombardment of a surface causes the emission of secondary electrons. Metals generally have a secondary electron emission coefficient of less than 0.1 under ion bombardment[5][31] while secondary electron emission coefficients of oxide surfaces is higher. Secondary electron emission from electron bombardment[32] is much higher than from ion bombardment.

Energetic ion bombardment of a surface can cause physical sputtering of surface material (Sec. 6.2). If the bombarding species are chemically reactive they can form a compound layer on the surface if the reaction products are not volatile. If this surface layer is electrically insulating or has different electrical properties than surrounding surfaces, surface charges can be generated that cause arcing over the surface. If the reaction products are volatile then plasma etching of the surface occurs.[33]

4.3.4 Gas Diffusion into Surfaces

The adsorption of gaseous species on a surface exposed to a plasma is poorly understood but one would expect that adsorption in a plasma would be greater than in the case of gases due to the presence of radicals, unique species, image forces, surface charge states on insulators, and other such factors. This may be a very important factor in reactive deposition processes.[34]

Absorption of a gas into the bulk of the material involves adsorption, possibly molecular dissociation, then diffusion into the material. The process of injecting gas into a surface is called "charging." Diffusion of gases, particularly hydrogen, into metals can be enhanced by exposure to a hydrogen plasma and low energy ion bombardment.[35][36] Reasons for the rapid absorption of hydrogen into surfaces include:

- There is no need for molecular dissociation at the surface
- Surface cleaning by the hydrogen plasma
- Implantation of accelerated hydrogen ions into the surface producing a high chemical concentration thus increasing the "chemical potential" which is the driving force for diffusion

4.4 CONFIGURATIONS FOR GENERATING PLASMAS

In generating and sustaining plasmas, energy is imparted to electrons by an electric field and the energetic electrons create ionization by electron-atom impact.

4.4.1 Electron Sources

Electrons in a plasma originate from: (1) secondary electrons from an ion or electron bombarded surfaces (secondary electron emission), (2) ionizing collisions, and (3) electrons from a thermoelectron emitting source (hot cathode).

4.4.2 Electric and Magnetic Field Effects

Electric fields are formed around solid surfaces that have a potential on them. The locations in space that have the same potential with respect to the surface are called equipotential surfaces. When the surface is flat or nearly so, the equipotential surfaces will be conformal with the solid surface. When the solid surface has a complex morphology, the equipotential surfaces will not be able to conform to the solid surface configuration and will "smooth-out" the irregularities. Surfaces with closely-spaced features, such as an open mesh (high transmission) grid, appear as a solid surface to the electric field. The separation between the equipotential surfaces establishes the electric field gradient. Electrons and ions are accelerated normal to the equipotential surfaces. Figure 4-2 shows some equipotential surfaces and the effects of curvature on the bombardment of surfaces by ions.

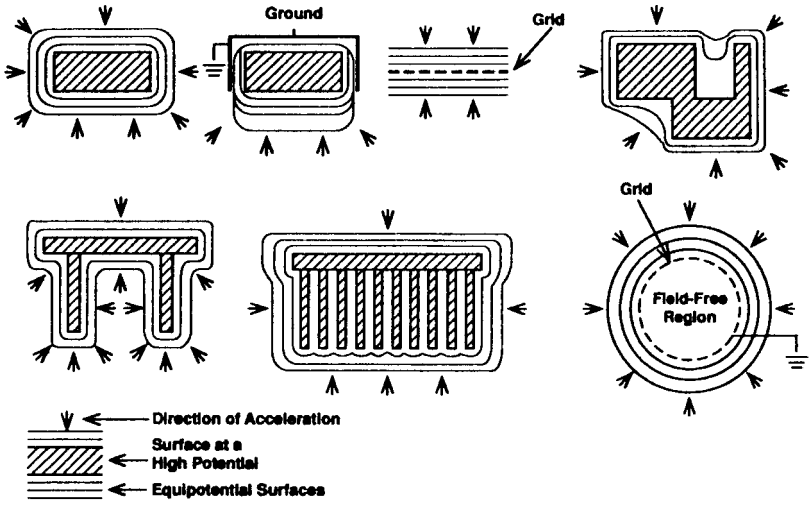


Figure 4-2. Equipotential surfaces and ion bombardment around various solid surfaces.

Magnetic fields in space can be generated in a number of ways including:

- Internal fixed permanent magnets
- External electromagnets
- Internal moving permanent magnets
- External permanent magnets

When using permanent magnets care must be taken to ensure that the magnetic field strength does not degrade with time. This is particularly a problem if the magnets are heated. The magnetic field distribution in space can be measured using Hall-effect probes. Figure 4-3 shows some magnetic field configurations.

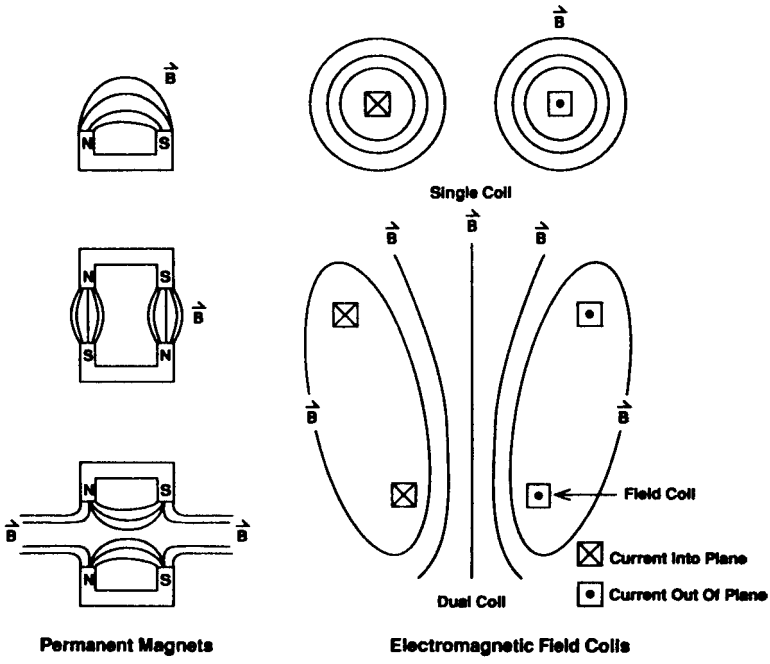


Figure 4-3. Magnetic field configurations.

Electrons, and to a lesser extent ions, will be affected by the magnetic field and magnetic field strength. If the electron path is parallel to the magnetic field lines, the electron will not be affected by the magnetic field. However, if there is any component of the electron trajectory that is normal to the magnetic field line the electron will spiral around the field lines. If the electron trajectory is normal to the magnetic field the electron will be trapped in a closed path. The higher the magnetic field strength the more rapid the circulation and the smaller the diameter of the orbit. This is the basis for the high frequency Klystron tubes developed during World War II.[37]

Low strength (50–500 gauss) magnetic fields affect the motion of electrons but not ions. In a vacuum, an electron with a velocity vector perpendicular to the magnetic field vector is confined to a circular path around the magnetic field lines with a radius, r, (gyro radius) and a frequency, ϕ, (gyro frequency) given by

$$r = M\, v_p / e\mathbf{B}, \quad \phi = e\mathbf{B}/M$$

where M = mass
v_p = velocity perpendicular to magnetic field
$\mathbf{B}$ = magnetic field strength
e = charge

If there is both an electric, **E**, and magnetic, **B**, field present, then the electrons have a drift velocity perpendicular to the **E x B** plane in addition to spiraling around the magnetic field lines. If there is a gas present, collisions cause the electrons to be scattered from their spiral path. After scattering the electrons begin a new spiral path. The electrons will tend to be trapped where the **E** and **B** fields are normal to each other and this will be the region of maximum ion density. These ions will repulse each other due to electrostatic effects and be accelerated to the cathode surface by the electric field.

4.4.3 DC Plasma Discharges

The cold cathode DC diode discharge operates in the abnormal glow discharge region where the cathode current density depends on the applied voltage. Figure 4-4 shows a DC diode discharge configuration and the potential drop across the interelectrode space. The cathode fall region is where most of the potential drop in a DC discharge is to be found.

Figure 4-4(*a*) shows the cathode dark space, the plasma region and possible substrate positions. The plasma potential with respect to ground is shown in (*b*). Note: that almost all of the applied potential is across the cathode fall region. Substrates may be positioned either at a position on the anode (ground) or at an "off-axis position" to avoid bombardment by secondary electrons accelerated away from the cathode.

In the DC diode discharge the cathode (negative) potential attracts ions from near the edge of the plasma region and they are accelerated across the cathode fall region to impinge on the cathode. The impinging ions and energetic neutrals, produced by charge exchange collisions, cause

the ejection of secondary electrons which are then accelerated back across the cathode fall region and create ions which sustain the discharge. Thus under equilibrium conditions, enough electrons are produced to create enough ions to create enough electrons to sustain the discharge. If conditions, such as potential, gas species, or gas pressure change, the equilibrium conditions will change. The energetic ion bombardment of the cathode surface also results in physical sputtering.

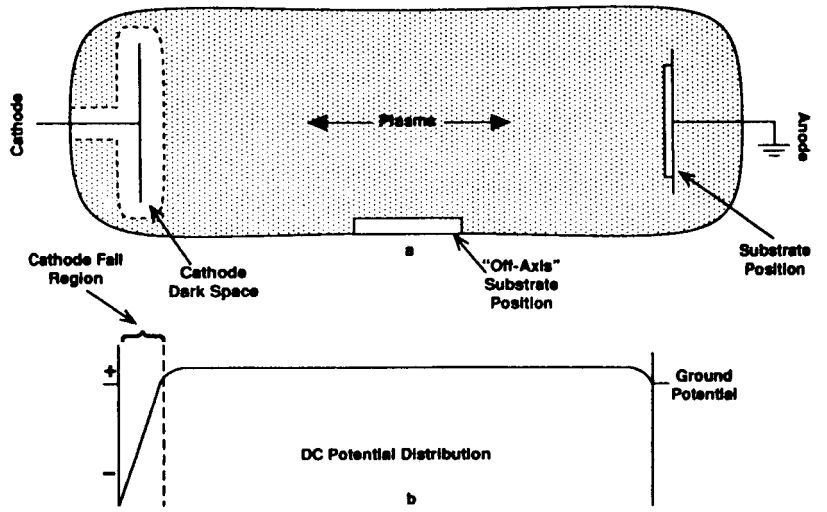


Figure 4-4. Direct current (DC) diode discharge.

The ions being accelerated to the cathode will experience physical collisions in the gas phase and lose some of their energy. Some of the ions being accelerated to the cathode may become neutralized by charge-exchange processes and this produces a spectrum of high energy neutral species. The result is a spectrum of high energy ions and neutrals bombarding the cathode with few of the ions reaching the surface with the full cathode fall potential. The energetic neutrals formed are not affected by the electric field and may bombard non-electrode surfaces near the target causing sputtering and film contamination. The DC diode configuration requires that the cathode be of an electrically conductive material since a dielectric cathodic surface will buildup a positive surface charge that will prevent further high energy bombardment.

The electrical current measured in the DC diode circuit is the sum of the ion flux to the target and the secondary electron flux away from the surface. Therefore the cathode current density and applied cathode voltage do not specify the flux and energy of the impinging ion current! However these measurements (along with gas pressure) are typically used to establish and control the plasma conditions. Often the discharge specification is in watts per cm^2 of the cathode surface. Most of the bombardment energy goes into cathode heating, requiring active cooling of the cathode in most cases.

When the DC discharge is first ignited at a constant pressure and voltage, there is a decrease in cathode current with time. This is due to removing the oxides, which have a high secondary electron emission coefficient, from the cathode surface, and heating of the gas which reduces its molecular density. The plasma is not in equilibrium until the discharge current becomes constant.

In the DC diode configuration the secondary electrons that are accelerated away from the cathode can reach high energies and impinge on the anode or other surface in the system. This can give rise to extensive heating of surfaces in the DC diode system. In the DC diode discharge configuration the plasma-generation region is primarily near the cathode; however the plasma fills the contained volume. This plasma can be used as a source of ions for bombardment, or for activation of reactive species.

In order to sustain a discharge, the secondary electrons must create enough ions to sustain the discharge. If the anode or ground surface is brought too close to the cathode the discharge is extinguished. The pressure-separation relationship that defines the separation is called the Paschen curve and is shown in Fig. 4-5. This effect can be used to confine the DC discharge to areas of the cathode surface where bombardment is desired by using a ground shield in close proximity to surfaces where bombardment is not desired. For example, in argon at about 10 microns pressure, the minimum separation is about 0.5 centimeters. If a ground shield is closer than this to the cathode, the discharge is extinguished between the surfaces.

Shields near the high voltage electrode cause curvature of the equipotential lines in the vicinity of the shields as shown in Fig. 4-2. This field curvature can result in focusing or diverging of the electron or ion trajectories since charged species are accelerated in directions normal to the field lines. This focusing can affect the heating and sputter erosion pattern on the cathode surface.

In a hot cathode DC diode discharge, hot thermoelectron-emitting surfaces at a negative potential, emit electrons that provide the electrons to

sustain the discharge.[38] This configuration can also use the electrons to evaporate material for deposition.[39][40] The hot cathode discharge can be operated at a lower pressure than the cold cathode DC discharge since the electron flux does not depend on the ion flux. Very high plasma densities can be achieved in a hot cathode system.

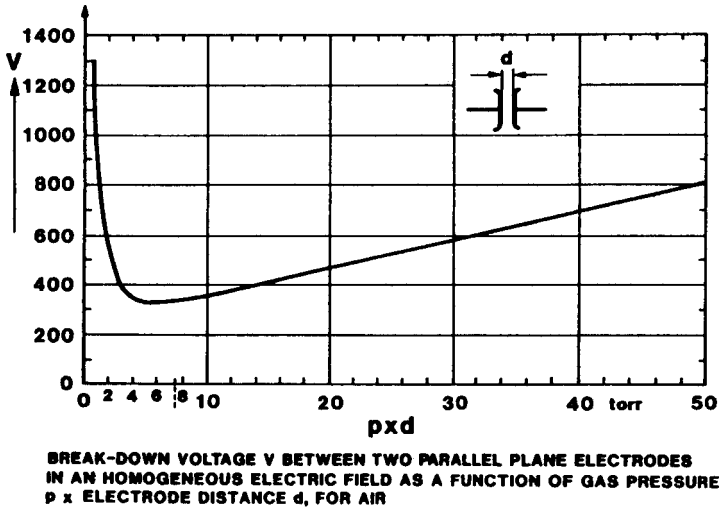


Figure 4-5. Paschen curve.

In the triode configuration the plasma is established between a cathode and anode and ions are extracted from the plasma by a third electrode using a DC or rf potential to give bombardment of a surface.[41][42] The triode configuration suffers from a nonuniform plasma density along its axis particularly if high currents of ions are being extracted—this results in nonuniform bombardment of a biased surface. Often the triode system uses a hot cathode and the electrons are confined by a weak magnetic field (50–500 gauss) directed along the anode-cathode axis. The triode configuration, using a mercury discharge, was used by Wehner for his early studies on physical sputtering.[43][44] Figure 4-6 shows a triode discharge used in a "barrel ion plating" configuration.[45]

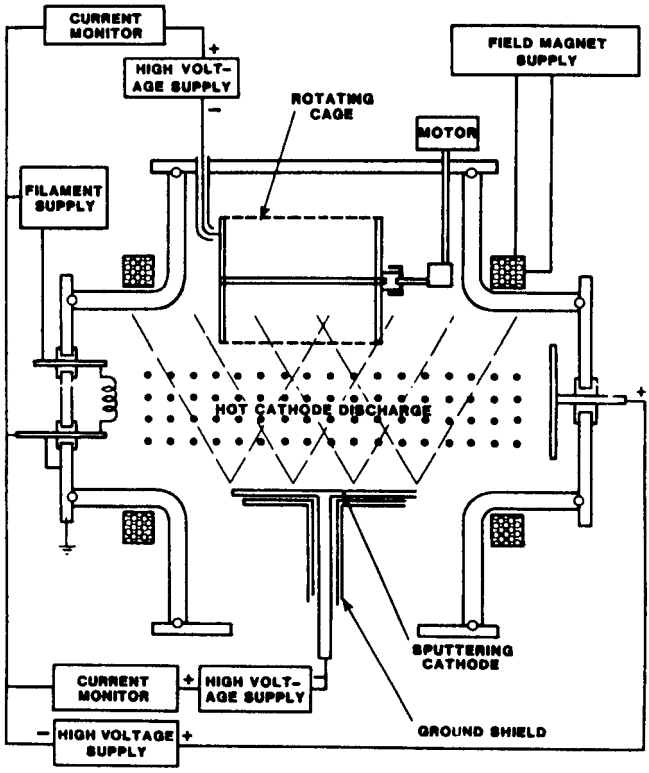


Figure 4-6. Barrel ion plating system configuration with a triode DC discharge.

The DC diode discharge cannot be used to sputter dielectric target materials, since charge buildup on the cathode surface will prevent bombardment of the surface. If there are reactive gases in the plasma their reaction with the target surface can lead to the formation of a surface that has a different chemical composition than the original surface. This change in composition leads to "poisoning" of the cathode surface and thus changes the plasma parameters. In the extreme, poisoning will cause bombardment of the cathode to cease due to surface charge buildup. If an insulating surface forms on the DC cathode, charge buildup will cause arcing over the surface.

The suppression of arcs generated in the DC discharge (arc suppression) are important to obtaining stable performance of the DC power supplies particularly when reactively sputter depositing dielectric films.[46] Arcing can occur anytime a hot (thermoelectron emitting) spot is formed or when surface charging is different over surfaces in contact with the plasma. Arc suppression is obtained by momentarily turning off the power supply or by applying a positive bias when an arc is detected.

Pulsed DC

When a continuous DC potential is applied to a metal electrode completely covered with a dielectric material, the surface of the dielectric is polarized to the polarity, and nearly the voltage, of the metal electrode. If the surface potential is negative, ions are accelerated out of the plasma to bombard the surface giving sputtering, secondary electron emission, "atomic peening," and heating. However, since the secondary electron emission coefficient is less than one the surface will buildup a positive surface charge and the bombardment energy will decrease then bombardment will crease. This problem can be overcome by using a pulsed DC rather than a continuous DC.

Pulsed DC uses a potential operating in the range 50–250 kHz where the voltage, pulse width, off time (if used), and pulse polarity can be varied.[47] The voltage rise and fall is very rapid during the pulse. The pulse can be unipolar, where the voltage is typically negative with a no-voltage (off) time, or bipolar where the voltage polarity alternates between negative and positive perhaps with an off time. The bipolar pulse can be symmetric, where the positive and negative pulse heights are equal and the pulse duration can be varied or asymmetric with the relative voltages being variable as well as the duration time.[48] Figure 4-7 shows some DC waveforms. Generally in asymmetric pulse DC sputter deposition, the negative pulse (e.g., -400 V) is greater than the positive pulse (e.g,. +100 V) and the negative pulse time is 80–90% of the voltage cycle and the positive pulse is 20–10% of the voltage cycle.

In pulse DC sputtering, during the positive bias (and off-time), electrons can move to the surface from the plasma and neutralize any charge build-up generated during the negative portion of the cycle. During the negative portion of the cycle, energetic ion bombardment can sputter dielectric surfaces.

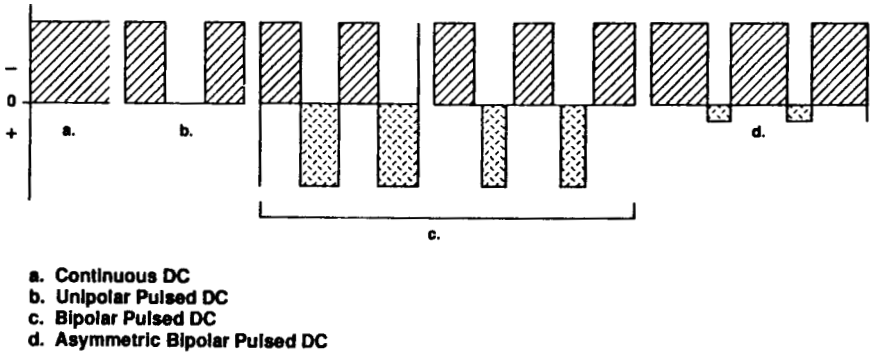


Figure 4-7. DC waveforms.

Pulsed DC power can be obtained by switching a continuous DC or sinewave power supply with auxiliary electronics[49] or can be obtained from a specially designed pulsed power supply that generally allows more flexibility as to waveform. The pulsed power supply generally incorporates arc suppression that operates by turning off the voltage or by applying a positive voltage when the arc initiates. Pulsed plasmas are also of interest in plasma etching and plasma enhanced CVD (PECVD).[50]

4.4.4 Magnetically Confined Plasmas

Balanced Magnetrons

In surface magnetron plasma configurations the electric (**E**) (vector) and magnetic (**B**) (vector) fields are used to confine the electron path to be near the cathode (electron emitting) surface. An electron moving with a component of velocity normal to the magnetic field will spiral around the magnetic field lines and its direction will be confined by the magnetic field. The frequency of the spiraling motion and the radius of the spiral will depend on the magnetic field strength. The interaction of an electron with the electric and magnetic fields depends on the magnitude and vector orientation of the fields (**E x B**). For example, if the magnetic field is parallel to a surface and the electric field is normal to the surface an electron leaving the surface will be accelerated away from the surface and

will spiral around the magnetic field. There will also be a resulting motion of the electron normal to the **E x B** plane (**E x B** drift). If the magnetic field is shaped in such a way as to allow a closed path for these electrons moving normal to the magnetic field then a "circulating current" is established on the surface. This circulating current may be several times the current measured in the external electrical circuit. The plasma thus formed is confined near the cathode surface.

In magnetron sputtering configurations the surface can be planar,[51][52] a post or cylinder,[53] a cone[54] or any surface of revolution. Figure 4-8 shows some surface magnetron configurations for confining electrons near a surface. Electron-atom collisions (and ionization) in a gas environment form a plasma near the surface. Using a magnetron configuration, plasmas can be sustained at a few tenths of a mTorr in argon. The magnetron is typically driven with a continuous or pulsed DC potential.

Magnetic fields can be generated using permanent magnets or electromagnets (Sec. 4.4.2). Permanent magnets have the advantage that they may be placed so as to position the field lines in a desirable manner; that is harder to do with electromagnets. Electromagnets may be used in a two-coil Helmholtz arrangement to produce a space with nearly parallel magnetic field lines. Magnetic polepieces may also be used to give nearly parallel magnetic field lines. Magnetic fields pass easily through nonmagnetic materials, such as aluminum, but magnetic materials must be "saturated" before the magnetic field can penetrate through them.

A major problem in using magnetic fields is the difficulty in obtaining a uniform field over a surface. This nonuniformity in the magnetic field produces a nonuniform plasma. This plasma nonuniformity means nonuniform bombardment of the cathode surface and nonuniform sputtering of the cathode material. In order to increase uniformity the plasma can be moved over the target surface by moving the magnetic field or the target surface may be moved in the magnetic field.

An rf bias can be superimposed on the continuous DC potential in order to establish a plasma away from the cathode. This is useful in ion plating and reactive sputter deposition where the plasma is used to activate the reactive species and provide ions for concurrent ion bombardment of the growing film. When an rf bias is used with a DC power supply, there should be an rf choke in the DC line to prevent rf from entering the DC power supply.

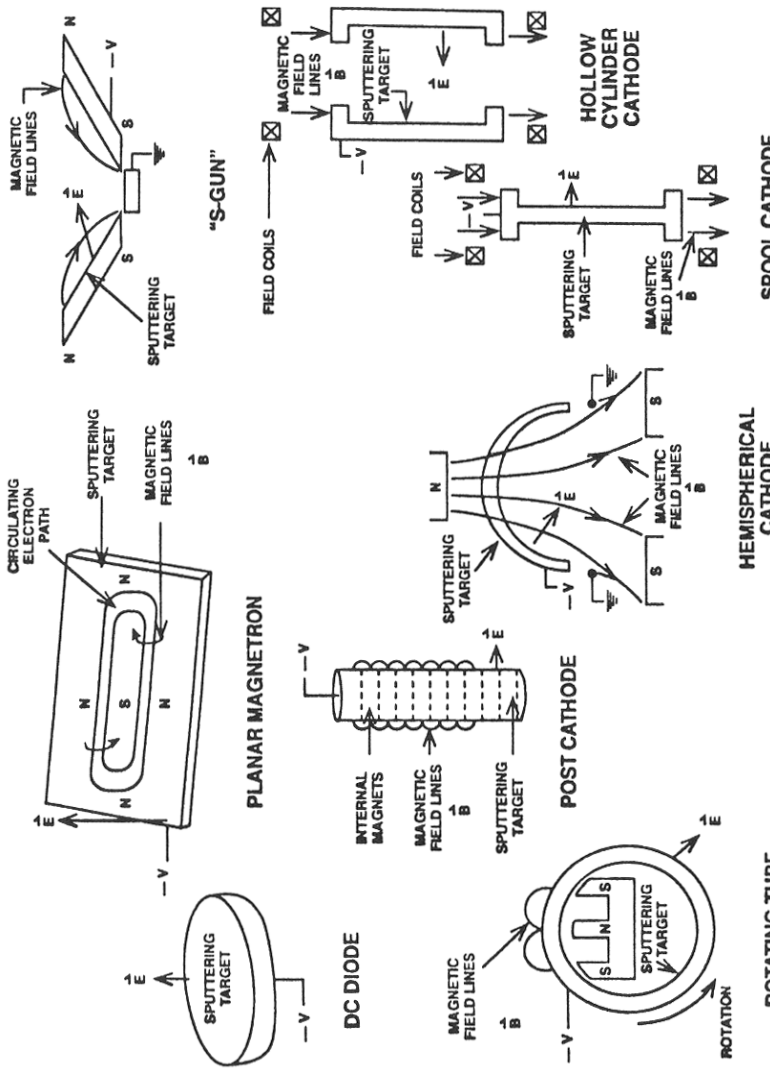


Figure 4-8. Surface magnetron configurations.

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Unbalanced Magnetrons

"Unbalanced magnetron" is the term given to magnetic configurations where some of the electrons are allowed to escape.[55]-[57] Most magnetrons have some degree of "unbalance" but in the application of unbalanced magnetrons, the magnetic fields are deliberately arranged to allow electrons to escape. These electrons then create a plasma away from the magnetron surface. This plasma can then provide the ions for bombardment of the substrate during ion plating and/or can activate a reactive gas of reactive deposition processes. The magnetic field for unbalancing the magnetron configuration can be supplied either by permanent magnets or by electromagnets. Some unbalanced magnetron configurations are shown in Fig. 4-9.

Unbalanced magnetrons are often used in a dual arrangement where the escaping field of the north pole of one magnetron is opposite the south pole of the other magnetron. This aids in trapping the escaping electrons. The escaping electrons are further trapped by having a negatively biased plate above and below the magnetrons.

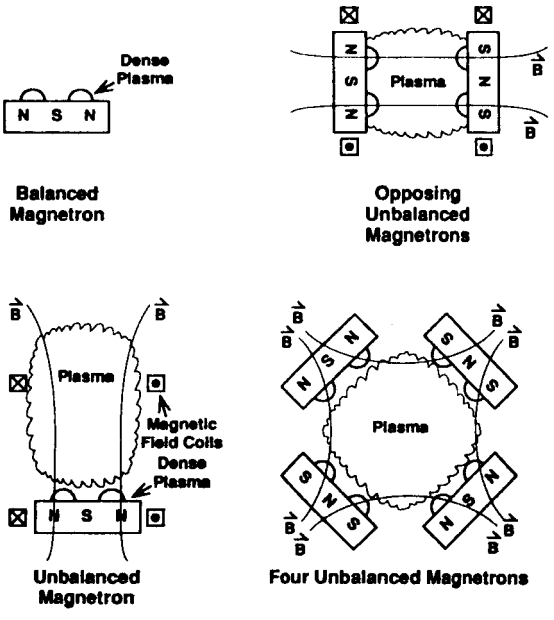


Figure 4-9. Balanced and unbalanced planar magnetron configurations.

4.4.5 AC Plasma Discharges

At low frequencies up to about 50 kHz alternating current (AC) discharges have essentially the same structure as DC discharges.[58][59] AC discharges are sometimes used in a dual electrode (target) arrangement where the electrodes are alternately biased positively and negatively (Sec. 6.6.3).

4.4.6 Radio Frequency (rf) Capacitively-Coupled Diode Discharge

In a capacitively-coupled radio frequency (rf) discharge, the electrons are caused to oscillate in the gas between the rf electrodes, thus gaining energy as shown in Fig. 1-2. The plasma acts as a low density electrical conductor and the rf field penetrates some distance into the plasma thus generating ions and electrons throughout the space between the electrodes. In the rf diode system the plasma generation region is primarily between the electrodes. At high frequencies the massive ions only respond to the time-averaged electric field while the electrons move to and away from the electrodes creating high sheath potentials. The plasma will always be positive with respect to large area electrodes and other surfaces.

The rf region extends from a low frequency of a few kilohertz to the microwave frequency band (about 1 GHz). Typically rf systems operate at 13.56 MHz or at harmonics thereof, with peak-to-peak voltages of greater than 1000 volts and power of up to 10 watts/cm^2 on the electrodes. The potential that appears at the surface of the driven electrodes in a parallel plate arrangement depends on the relative areas of the electrodes. In addition to the bias imposed by the rf field, a DC bias can be imposed on the surface by placing a blocking capacitor in the rf circuit or by having a DC potential applied from a DC source through an rf choke if the area of the grounded walls in contact with the plasma is large, i.e., if the plasma potential is determined by the grounded walls.

The conductance and capacitance of the discharge can be determined[60] and the rf potentials in the plasma volume can be determined using capacitive probes.[61] Typically an rf discharge is established at 0.5–10 mTorr and has an electron density of 10^9–10^{11}/cm^3.[62] The actual power input to the plasma is lessened by losses such as impedance mismatch which causes power to be reflected back into the power supply and coupling to surfaces in the system. Note that plasma shields, as used with DC discharges cannot be used

with an rf electrode because the rf couples into the shield. Keep all ground surfaces at least 10 Debye lengths from the rf electrode (i.e., further away the lower the pressure). Reference 63 indicates a method of determining how much power is actually coupled into the plasma.

Impedance matching networks are used to couple the maximum amount of power into the plasma by reducing the reflected power. The matching network should be placed as close as possible to the rf electrode and connected to the electrode with low capacitance and low inductance leads. The matching networks can be manually tuned or self-tuned. Avoid ground loops in the electrical circuits, i.e., ensure that each power unit is independently tied to a common ground and not to each other.

Radio frequency driven electrode surfaces immersed in a plasma assume a self bias with respect to ground. This bias depends strongly on the electrode configurations and the capacitance in the circuit. For the case of the symmetric rf diode system, where the electrodes are of equal area and there is no capacitance in the circuit, the plasma potential is slightly more positive than the positive electrode. If, on the other hand, the electrode areas are unequal in size (e.g., one leg is grounded), there is a capacitance on one branch of the external electrode circuit and the rf circuit is asymmetric. In the asymmetric discharge, the electrode having the smaller capacitance (e.g., smaller area) has a higher negative potential with respect to plasma than the other electrode and it is bombarded with higher energy ions.

In capacitively-coupled rf discharges, the plasma potential, and hence the sheath potential at the electrodes, can have a time-varying value of tens to hundreds of volts. When the electrodes have a different effective area, the plasma potential can also have a large DC potential with respect to one or more of the electrodes. These factors affect the distribution of ion energies incident on the electrode surfaces in an rf discharge.[64]-[66] The electrode potentials can be varied using an external capacitance.

The rf frequency extends from a few kilohertz to the high megahertz range. At the low end, the rf is used for induction heating as well as plasma generation (e.g., 400 kHz). Even though electrons and ions have differing masses (1:4000–100,000) at the low frequencies (<500 kHz) both the electrons and ions can follow the variations in electric fields. Above about 3 MHz the inertia of the ions prevent them from rapidly responding to the electric field whereas the electrons will still rapidly follow the electric field. A commercial rf frequency that is often used in rf plasma processing is 13.56 MHz. If the frequency is increased to above about 900 MHz the electrons will be unable to follow the electric field variations.

The frequency of the plasma discharge affects the DC sheath potential that is developed between the electrode and the plasma.[67][68]

When the rf electrode(s) are metal-backed insulators the metal-insulator-plasma acts as a capacitor and the surface potential that appears on the insulator surface alternates between a low negative potential and a high negative potential with respect to the plasma. Energetic ions are extracted from the rf plasma during the highly negative portion of the cycle and may be used to bombard and sputter the insulator surface. The rf plasma can be operated at pressures as low as 0.5 mTorr in argon, though at low pressures, high peak-to-peak voltages are required. If the electrode surface is to be a dielectric it must completely cover the conductive electrode surface. If the metallic conductor backing plate is exposed, the "capacitor" is effectively shorted. This is a common problem in sputter cleaning and plasma treatment of dielectric surfaces where the dielectric surface is placed on the metal surface without completely covering it.

4.4.7 Arc Plasmas

Vacuum arc plasmas are formed by passing a low voltage—high current DC current (arc) between closely-spaced electrodes in a vacuum. This arc vaporizes electrode material, allowing a plasma to form in the vapor between the two electrodes.[69] In the arc there is appreciable ionization of the material and many of the ions are multiply charged. It has been found that the ions from a vacuum arc have a high kinetic energy (50–75 eV for singly charged ions) due to a positive space charge formed above the cathode surface that accelerates the ions away from that region.

Gas arc plasmas are formed by passing a low voltage—high current DC current (arc) through a low pressure gas which vaporizes electrode material and allows a plasma to form in the gas/vapor mixture between the cathode and the anode.[69]-[71] In the arc, there is appreciable ionization of both the gas and the electrode material and many of the ions are multiply charged. Since there is a gas present, ions which are accelerated away from the space charge region are thermalized by collisions. In film deposition, it is common to accelerate the gas ions and the film ions to a substrate using an applied negative potential on the substrate. Cathodic arc film deposition processes use a solid water cooled cathode as the source of the depositing material while the anodic arc deposition process uses a molten anode for the vapor source.[72][73]

4.4.8 Laser-Induced Plasmas

Lasers can be used to vaporize surfaces and the laser radiation passing through the vapor cloud can ionize a high percentage of the vapor.[74]-[77] Laser vaporization is sometimes called laser ablation. Typically an excimer laser (YAG or ArF) is used to deposit energy in pulses. The YAG lasers typically deliver pulses (5ns, 5Hz) with an energy of about 1 J/pulse and the ArF lasers typically deliver pulses (20ns, 50Hz) with about 300 nJ/pulse. The deposited energy density can be greater than 5 x 10^{10} W/cm^2. The vaporized material forms a plume above the surface where some of the laser energy is adsorbed and ionization and excitation occurs. In laser vaporization the ejected material is highly directed.

4.5 ION AND PLASMA SOURCES

In most plasma processing, the surface being processed is usually in the plasma generation region. In other cases, it is desirable to produce the plasma in a plasma source and process the surface away from the plasma generation region. These plasma sources can provide the ions for bombarding the sputtering target in sputter deposition or the growing film in ion plating. They may provide the activated gaseous species desirable for reactive deposition processes or may provide dissociation of chemical vapor precursors to provide deposition from the vapor (ex., $CH_4 \rightarrow C$). Using plasmas for processing is often desirable because the presence of both ions and electrons prevent charge buildup on dielectric surfaces.

4.5.1 Plasma Sources

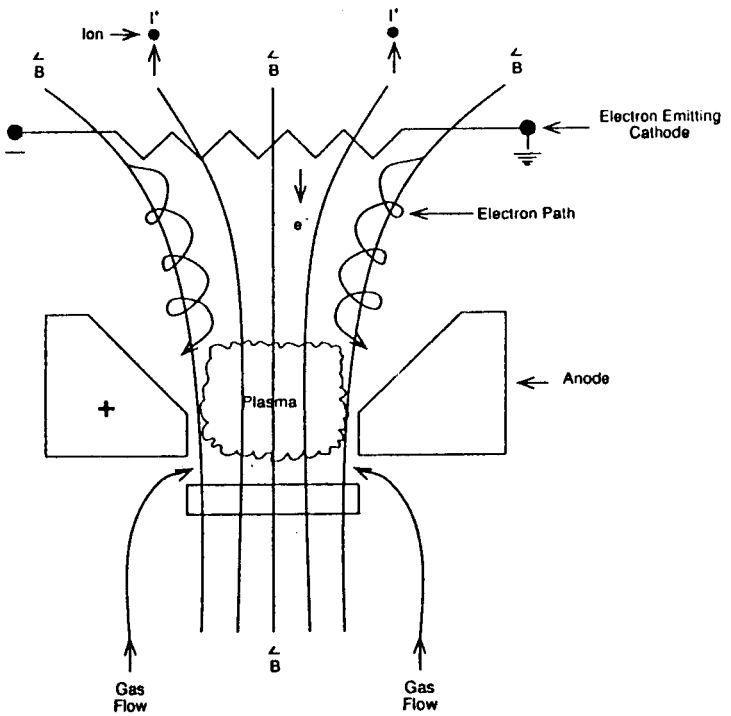
The plasma generated in a plasma source can be confined magnetically to form a plasma beam.[78] In a plasma, the electrons are easily "steered" using a magnetic field and the ions follow to maintain charge neutrality. Plasma sources may be "grid-less" which means that the particles in the beam will have a spectrum of energies or they may have extraction grids which allow more uniform ion energies.

End Hall Plasma Source

In the Hall-effect plasma source, electrons are steered by a magnetic field to pass through a gas stream to an anode surface as shown in Fig. 4-10 (*a*).[78]-[80] The grid-less Hall-type plasma source is usually operated at rather low voltages (30–100 eV) and provides ions with a wide distribution of energies. This type of source is often used to provide an oxygen plasma for reactive deposition of oxides.

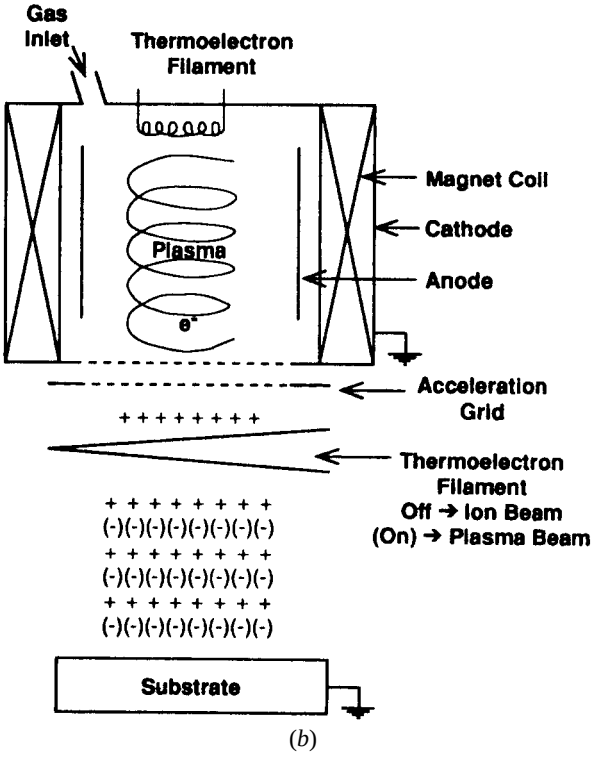
Hot Cathode Plasma Source

The Kaufman-type ion source[81] uses a thermoelectron emitter cathode, grid-extraction ion source that is often used as a plasma source by injecting electrons into the ion beam after it has been extracted from the ion gun as shown in Fig. 4-10 (*b*).



(*a*)

Figure 4-10. *(a)* End-Hall plasma source, *(b)* Kaufman plasma source.



(*b*)

Figure 4-10. (*Cont'd.*)

Another example of a hot cathode plasma source is the PISCES plasma generator[38] which uses a large-area heated lanthanum hexaboride or La-Mo electron emitter and magnetic confinement of the plasma. This source provides a large-area plasma source (70–80 cm^2) with a continuous current density of 6 x 10^{18} particles/cm^2-sec with an ion energy of 50–500 eV. The source was developed to test materials for use in TOKAMAK fusion reactors.

Capacitively Coupled rf Plasma Source

A parallel plate rf source an be used to form a linear plasma source as shown in Fig. 4-11 (*a*).[82] The rf frequencies typically range from 50kHz–13.56MHz.

Electron Cyclotron Resonance (ECR) Plasma Source

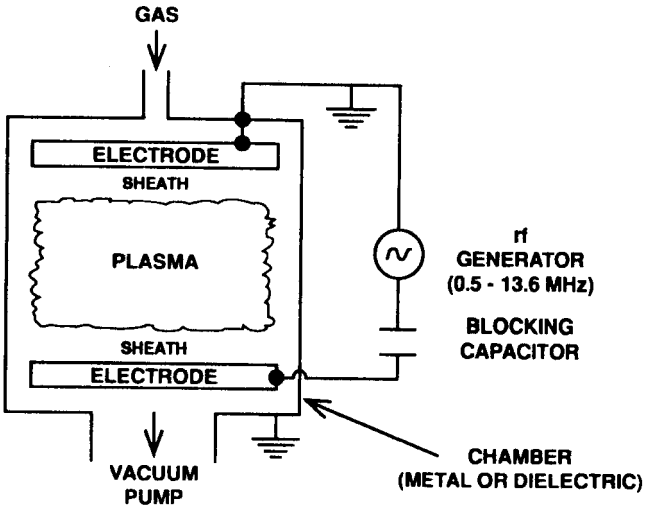
There is no sharp distinction between radio waves (rf) and microwaves but typically microwaves are in the gigahertz (10^9 Hertz) range with a wave length shorter than about 30 centimeters. A common industrial microwave frequency is 2.45 GHz. High frequencies (9.15 MHz–2.45 GHz) may be coupled with a magnetic field such that there is resonance coupling with circulating electrons to produce an Electron Cyclotron Resonance (ECR) plasma.[82]-[84] In these discharges, a cavity resonator with an axially varying magnetic field is used to effectively couple microwave energy into electrons by resonant adsorption. In the cavity, the electron density can be high (1 to 6 x 10^{11}/cm^3) and the electron temperature is relatively low (~10 eV) compared to the rf plasma. Figure 4-11(*c*) shows an ECR source.

The ECR discharge configurations may be of either a single pole (magnetic) cavity or a multi-pole (magnetic) cavity design. Single cavity systems form divergent fields. Multipole systems provide a more uniform field over a large area and higher electron densities. The ions from a multipole cavity are also more monoenergetic. The properties of an ECR plasma are very sensitive to reactor design. In order to spread the beam and maintain a uniform plasma density a "plasma bucket" can be used.[85]

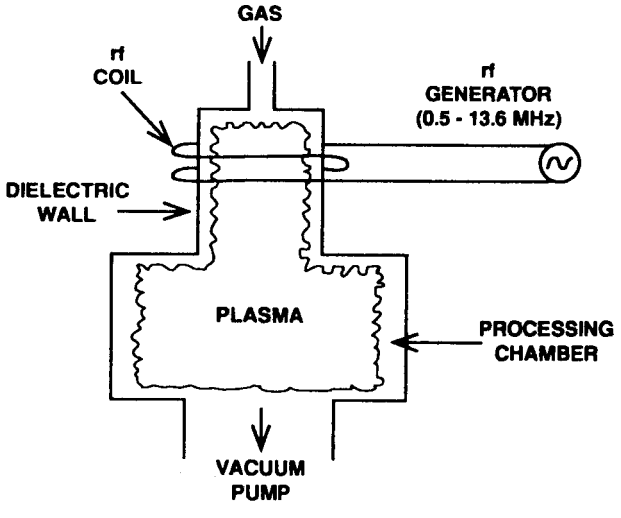
Typically an ECR discharge is established at 1 kW, 2.45 GHz, 800–1000 gauss, 0.1–10 mTorr gas pressure with an electron density of 10^{10}–10^{12} electrons/cm^3 and a self bias (plasma potential) of 10–20 volts in the remote substrate position. Auxiliary magnetic fields may be used in the vicinity of the substrate to increase plasma uniformity over the substrate surface. ECR sources suffer from the difficulty in scaling them up to large area sources.

Inductively Coupled rf Plasma (ICP) Source

Inductively coupled gas discharges are formed using frequencies from 400 kHz to 5 MHz generally applied to a coil surrounding a quartz tube holding the plasma which acts as a lossy conductor as shown in Fig. 4-11 (*b*).[86][87] Inductively coupled sources are amenable to scale-up to large area sources with high plasma enthalpy. The rf coil can be internal to the chamber to give an immersed coil source.[62]

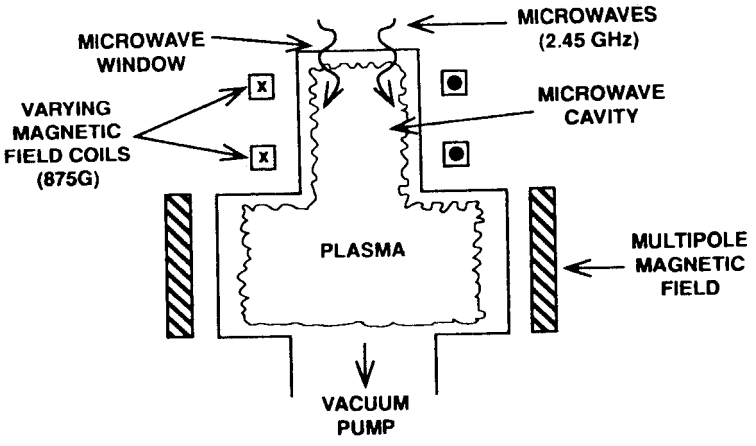


(*a*)

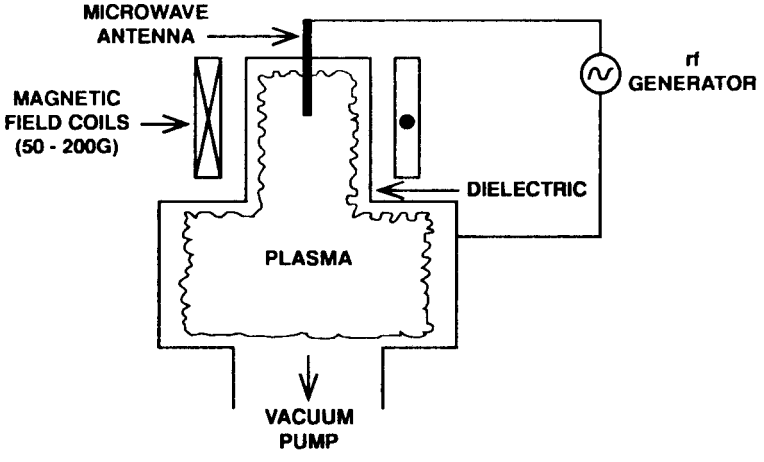


(*b*)

Figure 4-11. Plasma sources: (*a*) Parallel plate rf, (*b*) inductively coupled, (*c*) electron cyclotron resonance (ECR) discharge, (*d*) helicon discharge.



(*c*)



(*d*)

Figure 4-11. ***(Cont'd.)***

Helicon Plasma Source

In the helicon plasma source an rf-driven antenna radiates into a cylinder having a rather weak axial magnetic field as shown in Fig. 4-11 (*d*).[82] Resonant wave-particle interaction transfers the wave energy to the electron. The helicon plasma source can also be configured as a linear array of antennae to form a rectangular ion source.

Hollow Cathode Plasma Source

A hollow cathode can be used as a plasma source. When arrayed in a line, hollow cathodes can form a linear plasma source. For example, a linear hollow cathode array using oxygen gas and magnetic confinement of the plasma has been used to clean oil from strip steel.[87a][87b] It was found that a few percent CF_4 in the plasma increased the cleaning rate.

4.5.2 Ion Sources (Ion Guns)

Ion sources produce pure ion beams. Typically ions are produced in a plasma contained in a confined volume and ions extracted using a grid system which confines the electrons and accelerates the ions. This configuration can be used to generate ion beams with a rather well defined energy distribution and the source is called an ion gun. The ion gun sources allow the acceleration of ions to high energies in the grid structure. However the grid limits the current density that can be extracted. Often, after extraction, low-energy electrons are added to the ion beam to make a plasma beam (volumetrically neutral - space charge neutralization) to avoid coulombic repulsion in the beam ("space-charge blow-up") and surface change buildup. The plasma in the ion gun can be formed using a hot filament (Kaufman ion gun) (Fig. 4-10),[81][88] and immersed rf coil, an external rf coil, or and resonant cavity such as an ECR source. Ion sources developed for the fusion reactor program are capable of developing fluxes of 10^{18}–10^{19} ions/cm^2/sec over hundreds of square centimeters of extraction area. Typical ion guns for semiconductor etching, ion beam sputtering and ion assisted processing give <10 ma/cm^2 over tens of square centimeters of area.

In gun-type ion sources, inert gas ions, and ions of reactive species, both gaseous (N^+, O^+) and condensable (C^+, B^+) ions, may also be formed and accelerated. Molecules containing the species to be deposited can be fragmented, ionized, and accelerated in the plasmas. (e.g., SiH_4 can be fragmented, ionized, and accelerated to give deposition of a-Si:H and CH_4 may be fragmented, ionized, and accelerated and used to deposit carbon and diamond-like carbon films.[89])

Sources for forming ions of condensible species (film-ions) in vacuum began with the development of ion sources for isotope separation using mass spectrometers such as the Calutron, in the 1940's[90][91] and continues in the present. Commercial vacuum metal-ion beam sources have been developed using a pulsed arc vaporization source with a grid extraction system.[92]

Cesium (as well as Na, K, Rb) can be surface ionized (thermionic emission) from a hot tungsten surface (1200°C). A solid state cesium ion source is commercially available and does not use a plasma to form the ions. An alumino-silicate based zeolite (cesium mordenite) is heated to about 1000°C and cesium atoms diffuse to the surface of a porous tungsten electrode where they vaporize as negative ions. An electric field then accelerates then away from the surface. One gram of the zeolite provides about 20 coulombs of cesium ions (100 hours at 0.1 ma current). The cesium ions are used to sputter surfaces. When sputtering surfaces the negative cesium ions cause a high percentage of the sputtered particles to have a negative charge. This type of ion source is very UHV compatible.

4.5.3 Electron Sources

Electrons are used to heat surfaces and to ionize atoms and molecules. The most common source of electrons is a hot electron (thermoelectron) emitting surface. Generally the electron emitter is a tungsten or thoriated tungsten filament. Lanthanum hexaboride or La-Mo electron emitter surfaces can provide a higher electron emission for a given temperature than can tungsten.[6]

Plasma sources are often used as electron sources by magnetically deflecting the electrons. The hollow cathode electron source uses a plasma discharge in a cavity having a negative potential on the walls of the cavity which reflects and traps electrons thus enhancing ionization in the cavity. If the discharge in the cavity is a glow discharge and the walls are kept cool, the hollow cathode is called a cold hollow cathode and runs at

relatively high voltage and low currents. If the discharge is supported by thermoelectrons emitted from the hot walls it is called a hot hollow cathode and operates in an arc mode with low voltages and high currents.

In the cold hollow cathode source there is an anode grid surrounded by a cathode chamber. A DC discharge is established and an orifice allows the plasma beam to exit from the chamber. The discharge can also be operated using a hot filament in the anode chamber and augmented by a magnetic field.

In a hot hollow cathode source, the gas pressure in a tube is raised by having an orifice restricting the exit of gas from the tube and the thermoelectrons are trapped in the anode cavity.[93] A high density plasma beam exits the orifice and the electrons may be used to evaporate material or ionize gases. The hot hollow cathode is capable of much higher electron and ion densities than the cold hollow cathode system. The hollow cathode electron source can be used to augment plasma generation.[94][95]

4.6 PLASMA PROCESSING SYSTEMS

A good plasma system must first be a good vacuum system since contaminants will be activated in the plasma. In comparison to vacuum processing systems the plasma processing systems are complicated by:

- High gas loads from the introduction of processing gases
- Often a reduced pumping speed (gas throughput) in the deposition chamber
- Potentially explosive or flammable gases are used in some plasma-based processes

In many cases the generalized vacuum processing system shown in Fig. 3-8 may be used with a plasma in the processing chamber if the pumping system and fixturing is designed appropriately. Flow control for establishing the gas pressure needed to form a plasma, can be done by partially closing (throttling) the high vacuum valve, by using a variable conductance valve in series with the high vacuum valve or by the addition of the optional gas flow path as indicated. The electrode for forming the plasma ("glow bar") is positioned so as to extend into as large a region of the chamber as possible.

In plasma processing, the deposition conditions differ greatly depending on whether the substrate is placed on an active electrode, in the

plasma generation region or in a "remote position" where the plasma afterglow is found.

Plasma-based processes may either be clean or "dirty." Sputter deposition and ion plating are generally relatively clean processes while plasma etching and plasma-enhanced CVD are dirty processes. The main equipment-related problems in plasma-based PVD processing are:

- Production of a plasma having desirable and uniform properties in critical regions of the processing volume
- Control of the mass flow rate and composition of the gases and vapors introduced into the system
- Removal of unused processing gases, reaction products and contaminant gases and vapors from the processing volume
- Prevention of charge buildup and arcing
- Corrosion if corrosive gases or vapors are used in the processing

4.6.1 Gas Distribution and Injection

Plasma-based PVD deposition systems use a continuous gas supply. If the process gas(s) are inert, the method of injection is not very important except as related to vacuum gauge placement and local pressure variations such as the outlet of the injection port and the inlet to the pumping stack. However, if the processing gas is reactive and is being consumed in the processing, the gas injection pattern is very important in obtaining a uniform plasma.[96] It is important that the gas supplier meet specifications on the composition and purity of the processing gases so that the processing begins with a reproducible gas.[97] These specifications can include special tanks, distribution lines and fittings.

In a plasma system, the gas distribution system can be a source of particulates and water vapor. The first step in eliminating the impurities is to specify the necessary gas purity. Distribution of the gases should be in non-contaminating tubing such as Teflon™ or stainless steel. The stainless steel tubing used for distribution can be electropolished and passivated either by heating or by chemical treatments if water vapor is a concern. Inert gases can be purified at the point-of-use using hot chip purifiers. Particulates should be filtered (0.2 micron filters) from the gas at the point-of-use.

Gas Composition and Flow, Flow Meters, and Flow Controllers

Mass flow meters (MFM) and mass flow controllers (MFC) are discussed in Sect. 3.5.8. Gas mixtures are often used in PVD processing, particularly for reactive deposition processes. For example in the deposition of decorative and wear resistant coatings, the mixture may contain argon, nitrogen and a hydrocarbon gas such as acetylene (C_2H_2). When the system has a constant pumping speed for each of the gases being used, the partial pressures can be determined from the total chamber pressure and the individual mass flow rates.

In reactive deposition, the partial pressures of each of the reactive gases in the deposition chamber is an important process variable. If the pumping speeds are not the same for each gas or if reactive deposition is taking place, which removes some of the reactive gases by "getter pumping," then the partial pressures for each gas in the chamber must be determined by some in-chamber measurement technique. Such measurement and control techniques include: differentially pumped mass spectrometers, optical emission monitors (plasmas), and optical adsorption spectrometers. The amount of getter pumping will depend on the film area being deposited and the deposition rate as well as the plasma parameters. Changes in deposition area (loading factor) or deposition rate will affect the partial pressure of the reactive gas.

4.6.2 Electrodes

Electrodes in a plasma system are important in determining the plasma properties. For DC potentials, corners, edges, and points are high field regions. The curvature of the equipotential surfaces in such regions affects the acceleration of ions and electrons as shown in Fig. 4-2. High transmission grids (>50%) can be used in plasma systems to establish the position of equipotential surfaces as shown in the Fig. 4-2.

For rf potentials, the electrodes act as antenna broadcasting the electric field into the space around the electrode. The radiation pattern from the electrode is affected by its shape and shape is more important at the higher rf frequencies. This means that the plasma generation by the electrode is affected by its shape. The best electrode shapes are simple surfaces such as a flat plate. Complex surfaces may have to be surrounded by an open-grid structure in order to attain a uniform radiation pattern and

more uniform plasma generation. In some cases, it is desirable to prevent rf power from being coupled into a surface or into a region around a surface. The surface can be placed inside a metallic grid which forms a field-free region around the surface. This configuration is like the "etch tunnel" used in plasma etching.

4.6.3 Corrosion

Corrosion can be a problem in plasma systems that use corrosive or potentially corrosive processing gases. Corrosion can produce particulate contamination in the system as well as destroy sealing surfaces. Corrosion is a particular problem when using stainless steel or aluminum in the presence of chlorine. Pumps should be designed and built to handle corrosive gases/vapors and particulates. If corrosive gases and/or particulates are being pumped, the pump oils should be compatible with the gases/vapors and the pump oils should be routinely changed.

Heavily anodized aluminum is used in plasma systems exposed to chlorine plasmas which corrode stainless steel. After anodization, the anodized layer is densified by "sealing" using hot water containing nickel acetate or if heavy metal contamination is a concern, steam sealing can be used. The Hastalloy™ C-22 alloy is also used for chlorine environments. Monel™ and polymer-coated surfaces are used in some applications.

4.6.4 Pumping Plasma Systems

Pumping plasma systems can be done with any pump that can operate at the desired flow rate and pressure, that is compatible with the gases being used, and can handle the contaminants generated. Typical flow rates for plasma cleaning, sputter deposition, and ion plating are about 200 std-cm^3-min^{-1} (sccm).

4.7 PLASMA-RELATED CONTAMINATION

The plasma can be effective in forming, releasing, and activating contamination in the vacuum system. If low gas throughput is being used, the contaminant gases, vapors, and particulates are not readily pumped away. In order to aid in the removal of the contaminants, a "pump-

discharge-flush-pump" sequence can be used. In this operation, the system is pumped down to a low pressure, the conductance is decreased, and the pressure is raised so that a discharge can be established. The gas discharge desorbs the contaminants and when the pumping system is opened to full conductance the contaminants are pumped out of the system.

4.7.1 Desorbed Contamination

Plasmas enhance desorption from surfaces by ion scrubbing, photodesorption, and heating of surface due to radiation and recombination. Inert gas plasmas are used to desorb (ion scrub) contaminates such as water vapor. Reactive gases such as oxygen and hydrogen are used to chemically react with and volatilize contaminates such as hydrocarbons.

4.7.2 Sputtered Contamination

High energy neutrals that are reflected from the cathode or are formed by charge exchange processes can cause sputtering in undesired locations when there are low gas pressures in the plasma system. Contamination from fixtures, shutters, and other surfaces can occur. For example, if a stainless steel shield is used around a gold sputtering target, stainless steel will be sputtered and contaminate the gold film. In some cases, the surface being sputtered can be coated with the material being deposited so the sputtered "contaminant" is of the film material. Dielectric or electrically-floating surfaces can attain a high enough self-bias in the plasma system to be sputtered by ions accelerated from the plasma.

4.7.3 Arcing

Arcs can vaporize material and generate particulates in the plasma system. Arcing generally occurs over surfaces when a potential difference has been established due to plasma conditions. Arcing is particularly bad when depositing electrically insulating or poorly conducting films. Arcing can often be minimized by using pulsed DC rather than continuous DC or by adding an rf component to the DC plasma power source. Arcing can also occur over the electrical insulators in the feedthroughs if the insulators are coated by deposited film material. The feedthroughs should be shielded from depositing film material.

4.7.4 Vapor Phase Nucleation

Plasma-based PVD processing can produce ultrafine particles ("soot" or "black sooty crap" [BSC]) in the plasma region by vapor-phase nucleation thereby generating a "dusty plasma."[98] This is particularly true when using hydrocarbon precursors in the reactive deposition of carbides. These particles attain a negative charge and are suspended in the plasma near walls where they can grow to appreciable size.[99]-[101] Since the walls are also at a negative potential with respect to the plasma, particles will be suspended in the plasma. These particles can be monitored using scattered laser light techniques. Since the particles in the plasma have a negative charge, they will not deposit on the negatively-biased or grounded surfaces during deposition but will deposit on the chamber walls and the substrates when the plasma is extinguished and the self-bias disappears. These particulates should be swept through the vacuum pumping system as much as possible. This is best done by keeping the plasma on and opening the conductance valve to extinguish the plasma by rapidly reducing the pressure. The applied bias potential on surfaces should be retained until the plasma is extinguished. These particles can clog screens and accumulate in pump oils and the oils should be changed periodically.

4.7.5 Cleaning Plasma Processing Systems

Plasma systems are cleaned the same way as vacuum systems are cleaned. Removable shields and liners should be used wherever possible. Plasma systems used for PVD processing may have a large number of particulates generated during the processing from vapor phase nucleation, arcing, and flaking. Particulates should be removed using a dedicated vacuum cleaner with a HEPA-type filter system.

In some cases, the plasma system can be cleaning using *in situ* plasma etching. For example, when nitrides have been deposited in the system, the system can be cleaned using a plasma such as CF_4 or NF_3 which produces a lot of fluorine radicals.[102] Oxygen plasmas can be used to remove carbon and hydrocarbon contamination from the system.

4.8 SOME SAFETY ASPECTS OF PLASMA PROCESSING

Plasmas are electrical conductors and the presence of a high voltage anywhere in the system can allow un-grounded surfaces in contact with the plasma to attain a high voltage. For example, a metal chamber isolated from ground by a rubber gasket can attain a high potential if an ionization gauge is used in contact with the plasma. Make sure that all metal surface that are not meant to be electrodes are grounded in a plasma system.

There have been several explosions in plasma pumping systems when people try to pump pure oxygen through a system containing hydrocarbon pump oils. Compressing the pure oxygen in contact with the hydrocarbon oil is like making it a diesel engine. Vacuum pumps are not designed to be internal combustion engines. When pumping oxygen, make sure that the pump oils are compatible with oxygen or use a less-explosive oxygen mixture such as air. Hydrogen is extremely explosive and flammable and should be pumped with care. Forming gas, which is a mixture of hydrogen in nitrogen (1:9), is less dangerous than pure hydrogen.

When pumping some processing gases and vapors, the gases/vapors can accumulate in the pump oils decreasing their performance and perhaps presenting a safety hazard during maintenance and repair. In plasma etching, where relatively high gas pressures are used and numerous species can be formed in the plasma, care should be taken with the pump oil and exhaust since some of the species formed may be toxic, mutagenic, or carcinogenic. For example, if CCl_4 has been pumped in the presence of water vapor, phosgene ($COCl_2$), a highly toxic chemical warfare agent, can be produced and accumulate in the pump oil.

Concern has been expressed about the possibility of producing cyanide gas when using nitrogen and a hydrocarbon vapor in the reactive deposition of carbonitrides, but no evidence of significant levels of cyanide gas have ever been detected to my knowledge.

4.9 SUMMARY

In PVD processing a plasma is used as a source of ions and electrons as well as to activate reactive species for reactive deposition process. Plasmas are generated by electron-ion collisions giving ionization but there are many

configurations for generating and using plasmas. Typically one of the goals in plasma generation is to generate as highly ionized plasma as possible at a low gas density. This often involves using magnetic fields to control the path of electrons in the low pressure gas. A good plasma system must first be a good vacuum system since contaminants are activated in the plasma.

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5

Vacuum Evaporation and Vacuum Deposition

5.1 INTRODUCTION

Vacuum deposition (or vacuum evaporation), is a Physical Vapor Deposition (PVD) process in which the atoms or molecules from a thermal vaporization source reach the substrate without collisions with residual gas molecules in the deposition chamber. This type of PVD process requires a relatively good vacuum. Although sputtering and sputter deposition were reported in the mid-1800's using oil-sealed piston pumps, vacuum evaporation had to await the better vacuums provided by the Sprengel mercury-column vacuum pumps. In 1879 Edison used this type of pump to evacuate the first carbon-filament incandescent lamps and in 1887 Nahrwold performed the first vacuum evaporation. Vacuum deposition of metallic thin films was not common until the 1920's. Optically transparent vacuum deposited antireflection (AR) coatings were patented by Smakula (Zeiss Optical) in 1935.[1] The subject of vacuum evaporation was reviewed by Glang in 1970[2] and most review articles and book chapters on the subject since that time have drawn heavily on his work.

Vacuum deposition normally requires a vacuum of better than 10^{-4} Torr. At this pressure there is still a large amount of concurrent impingement on the substrate by potentially undesirable residual gases which can contaminate the film. If film contamination is a problem, a high

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(10^{-7} Torr) or ultrahigh ($<10^{-9}$ Torr) vacuum environment can be used to produce a film with the desired purity, depending on the deposition rate, reactivities of the residual gases and depositing species, and the tolerable impurity level in the deposit.

5.2 THERMAL VAPORIZATION

5.2.1 Vaporization of Elements

Vapor Pressure

The saturation or equilibrium vapor pressure of a material is defined as the vapor pressure of the material in equilibrium with the solid or liquid surface in a closed container. At equilibrium, as many atoms return to the surface as leave the surface. Vapor pressure is measured by the use of a Knudsen (effusion) cell which consists of a closed volume with a small orifice of known conductance. When the container is held at a constant temperature, the material that escapes through the hole depends on the pressure differential. With a vacuum environment outside the orifice and knowing the rate of material escaping, the equilibrium vapor pressure of the material in the container can be calculated. The vapor pressures of the elements have been presented in tabular and graphical form.[3] The Knudsen cell is often used as a source for Molecular Beam Epitaxy (MBE) where the deposition rate can be carefully controlled, by controlling the temperature of the source[4] or by mechanically interrupting the beam.[5]

Figure 5-1 shows the vapor pressure of selected materials as a function of temperature. Note that the slopes of the vapor pressure curves are strongly temperature dependent (about 10 Torr/100°C for Cd and 10 Torr/250°C for W). The vapor pressures of different materials at a given temperature can differ by many orders of magnitude. For vacuum deposition, a reasonable deposition rate can be obtained only if the vaporization rate is fairly high. A vapor pressure of 10^{-2} Torr is typically considered as the value necessary to give a useful deposition rate. Materials with a vapor pressure of 10^{-2} Torr above the solid are described as subliming materials and with a vapor pressure of 10^{-2} Torr above a liquid melt are described as evaporating materials. Figure 5-2 shows the equilibrium vapor pressure curves of lithium and silver in detail and shows that at 800 K (527°C) the vapor pressures differ by a factor of 10^7.

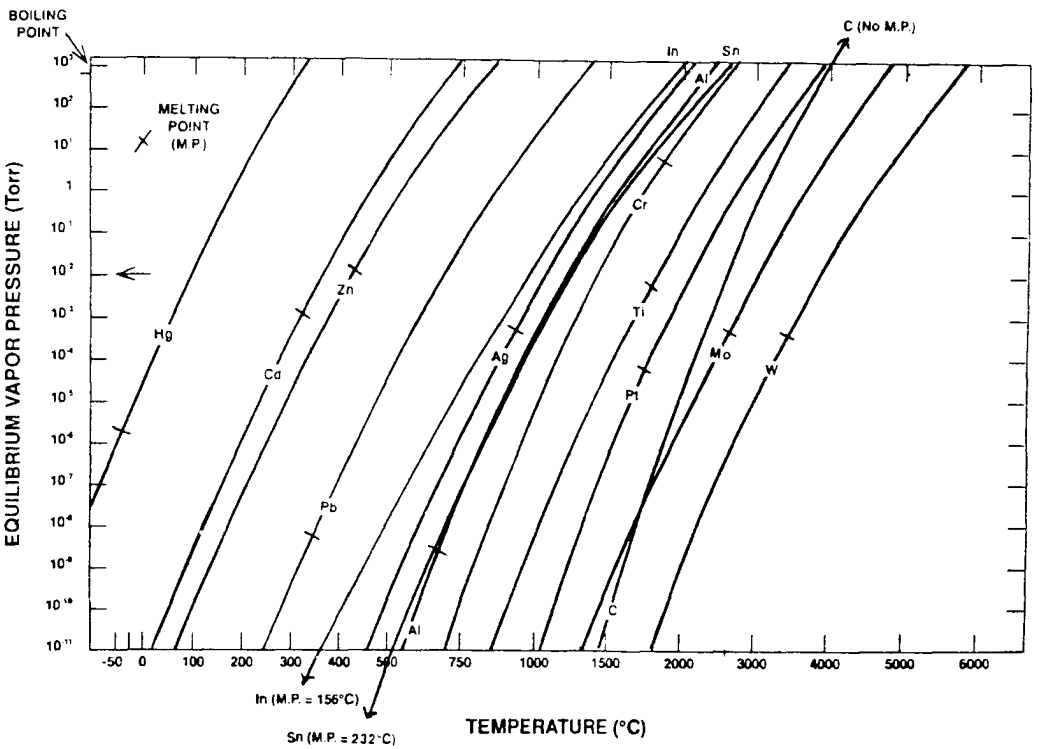


Figure 5-1. Equilibrium vapor pressure of selected materials. The slashes indicate the melting point (MP).

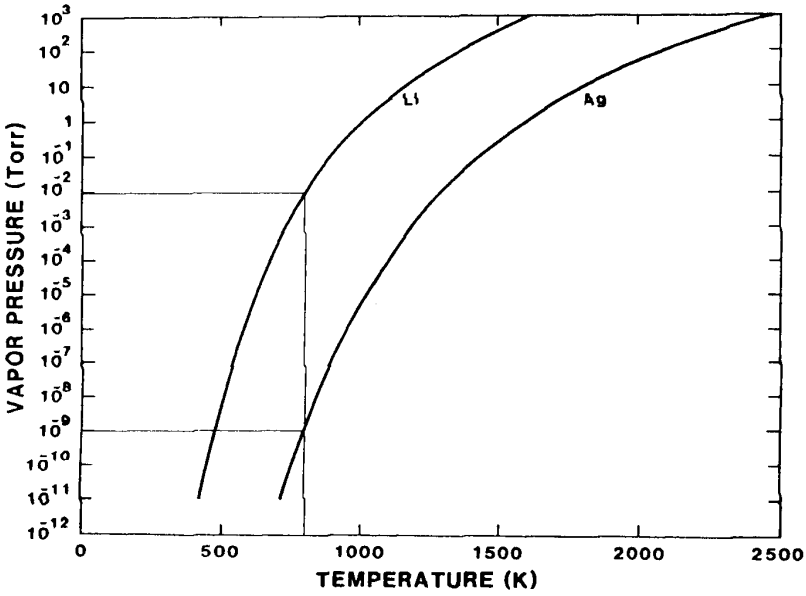


Figure 5-2. Equilibrium vapor pressure of lithium and silver.

Many elements evaporate, but many such as chromium (Cr), cadmium (Cd), magnesium (Mg), arsenic (As), and carbon (C) sublime, and many others such as antimony (Sb), selenium (Se), and titanium (Ti), are on the borderline between evaporation and sublimation. For example, chromium, which has a vapor pressure of 10^{-2} Torr 600°C below its melting point, is generally vaporized by sublimation. Carbon cannot be melted except under high hydrostatic pressure. Materials such as aluminum, tin, gallium, and lead have very low vapor pressures above the just-molten material. For example, tin has a vapor pressure of 10^{-2} Torr 1000°C above its melting point. Aluminum and lead have vapor pressures of 10^{-2} Torr at about 500°C above their melting points.

Most elements vaporize as atoms but some, such as Sb, Sn, C, and Se have a significant portion of the vaporized species as clusters of atoms. For materials which evaporate as clusters, special vaporization sources, called baffle sources, can be used to ensure that the depositing vapor is in the form of atoms. It should be noted that as a material is heated, the first

materials that are volatilized are high vapor pressure surface contaminates, absorbed gases, and high vapor pressure impurities.

A material vaporizes freely from a surface when the vaporized material leaves the surface with no collisions above the surface. The free surface vaporization rate is proportional to the vapor pressure and is given by the Hertz-Knudsen vaporization equation (Eq. 1):[2][6]

Eq. (1) $dN/dt = C\,(2\pi mkT)^{-1/2}\,(p^*-p)\ \text{sec}^{-1}$

where dN = number of evaporating atoms per cm^2 of surface area
C = constant that depends on the rotational degrees of freedom in the liquid and the vapor
p^* = vapor pressure of the material at temperature T
p = pressure of the vapor above the surface
k = Boltzmann's constant
T = absolute temperature
m = mass of the vaporized species

The maximum vaporization rate is when p=0 and C=1. In vacuum evaporation the actual vaporization rate will be $^1/_3{}^{rd}$ to $^1/_{10}{}^{th}$ of this maximum rate, because of collisions in the vapor above the surface (i.e., p>0 and C•1), surface contamination and other effects.[7] Figure 5-3 shows some calculated free-surface vaporization rates.

Flux Distribution of Vaporized Material

For low vaporization rates the flux distribution can be described by a cosine distribution.[2][6] With no collisions in the gas phase, the material travels in a straight line between the source and the substrate (i.e., line-of-sight deposition). The material from a point source deposits on a surface with a distance and substrate orientation dependence given by the cosine deposition distribution equation (Eq. 2). Figure 5-4 shows the distribution of atoms vaporized from a point source and the thickness distribution of the film formed on a planar surface above the point source based on Eq. 2.

Eq. (2) $dm/dA = (E/\pi r^2)\cos\phi\ \ \cos\theta$ (refer to Fig. 5-5)

where dm/dA is the mass per unit area
E = the total mass evaporated
r = the distance from the source to the substrate
θ = the angle from the normal to the vaporizing surface
ϕ = the angle from the source - substrate line

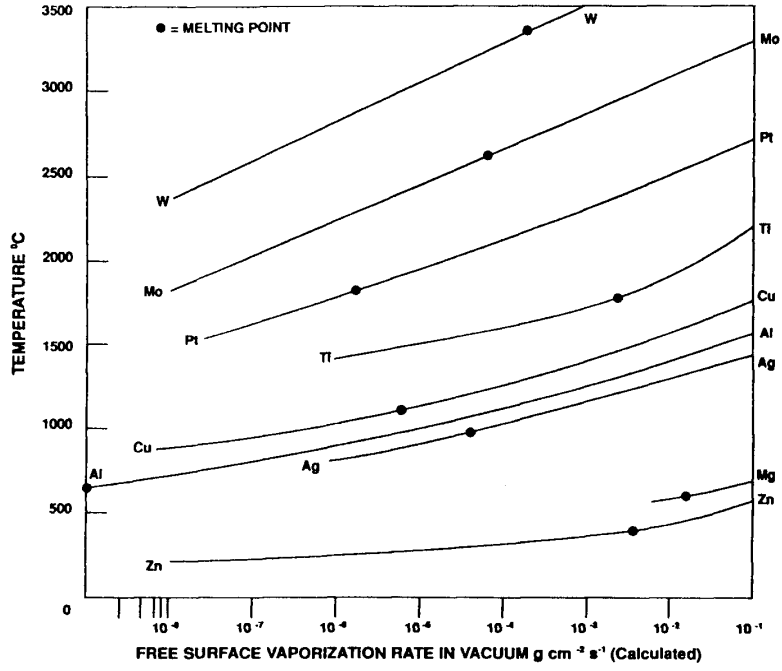


Figure 5-3. Free-surface vaporization rates.

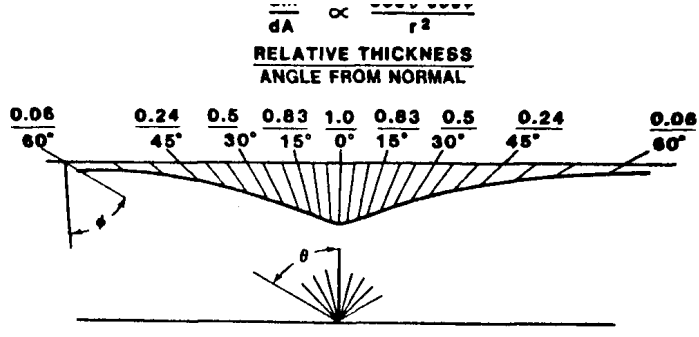


Figure 5-4. Distribution of atoms vaporized from a point source and the thickness distribution of the film formed on a planar surface above the source.

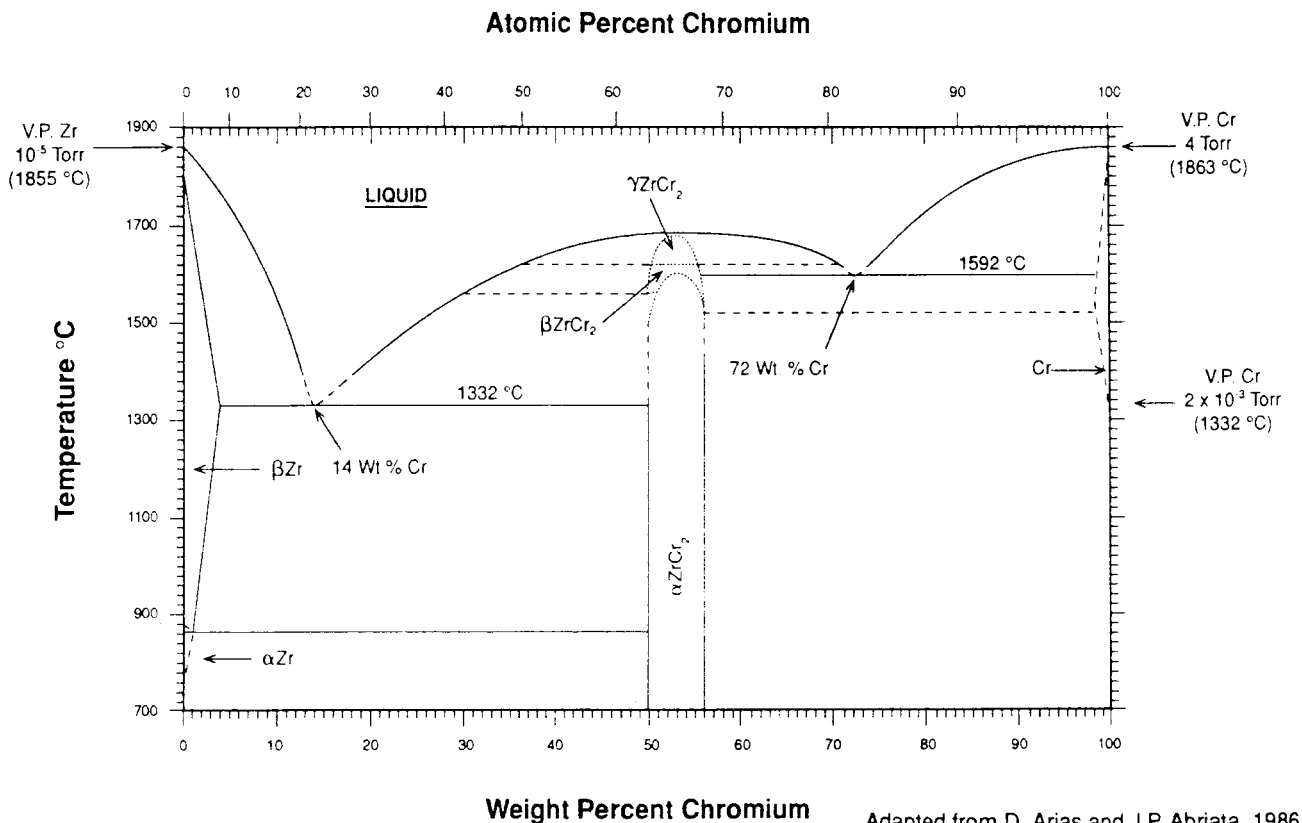


Figure 5-5. Cr-Zr phase diagram.

At any point on the surface the angular distribution of the depositing species is small since they originate from a point vaporization source. Generally the total area of vaporization in thermal evaporation is small, giving a small angular distribution of the incident atomic flux on a point on the substrate. In actuality, the flux distribution from a free surface may not be cosine but can be modified by source geometry, collisions associated with a high vaporization rate, level of evaporant in the source, etc. In such cases, the flux distribution must be measured directly.[8] A more complete model for the flux distribution from a Knudson (orifice) source is given by the Knudsen effusion model proposed by Ruth and Hirth.[9]

Atoms leave a hot surface with thermal energies given by $^3/_2\ kT$ where k is Boltzmann's constant and T is the absolute temperature.[2][6] The atoms have a Maxwell-Boltzmann distribution in velocities. For example, for a 1500°C evaporation temperature of copper, the mean kinetic energy of the vaporized copper atoms is 0.2 electron volts (eV) and the mean atom velocity is about 1 km/sec.

5.2.2 Vaporization of Alloys and Mixtures

The constituents of alloys and mixtures vaporize in a ratio that is proportional to their vapor pressures (i.e., the high vapor pressure constituent vaporizes more rapidly than the low vapor pressure material).[2][6] This relationship is called Raoult's Law and the effect can be used to purify materials by selective vaporization/condensation. When evaporating an alloy from a molten pool, the higher vapor pressure material steadily decreases in proportion to the lower vapor pressure material in the melt. For example, when evaporating an Al:Mg (6.27 at%) alloy at 1919 K, the Mg is totally vaporized in about 3% of the total vaporization time.[10][11]

Vaporization of alloys produces a gradation of film composition as the evaporant is selectively vaporized. This can be desirable or undesirable. For example, when a copper-gold alloy film is deposited on polymers by evaporation of a Cu-Au alloy, copper, which has a higher vapor pressure than gold, is deposited at a higher initial rate than the gold. This results in copper enrichment at the interface which is conducive to good adhesion between the deposited film and the polymer. When vaporizing alloy materials where one material is vaporizing faster than the other, it is sometimes possible to replenish the depleted constituent of the melt by using a feeding source such as a wire or pellet feeder.

In some cases. the nature of vaporization of an element can be changed by alloying it with another material. For example, chromium (MP=1863°C) which normally sublimes, can be alloyed with zirconium (MP=1855°C) to give a liquid melt as is shown in Fig. 5-5. The eutectic alloy of Zr:Cr (14 wt%) melts at 1332°C at which temperature chromium has a vapor pressure of ≈10^{-2} Torr and zirconium has a vapor pressure of ≈10^{-9} Torr. Another eutectic alloy of Zr:Cr (72 wt%) has a melting point of 1592°C.

5.2.3 Vaporization of Compounds

Many compounds, such as SiO, MgF_2, Si_3N_4, HfC, SnO_2, BN, PbS, and VO_2, sublime. Compounds often vaporize with a range of species from atoms, to clusters of molecules, to dissociated or partially dissociated molecules. For example, in the thermal vaporization of SiO_2, a number of species are formed in addition to SiO_2, for example, $(SiO_2)_x$, SiO_{2-x}, SiO, Si, O, etc. The degree of dissociation is strongly dependent on the temperature and composition of the compound.[12]

5.2.4 Polymer Evaporation

Many monomers and polymers can be evaporated producing thin organic films on a substrate surface. Some organic materials can be crosslinked in the vapor phase in a heated furnace before condensing on the substrate surface (paralyene process).[13] Condensed polymers can be crosslinked on the surface by exposing them to an electron beam[14] or ultraviolet radiation.[15]

5.3 THERMAL VAPORIZATION SOURCES

Thermal vaporization requires that the surface and generally a large volume of material must be heated to a temperature where there is an appreciable vapor pressure. Common heating techniques for evaporation/ sublimation include resistive heating, high energy electron beams, low energy electron beams and inductive (rf) heating.

5.3.1 Single Charge Sources

In most vacuum deposition applications a given amount of material (charge) is heated. In some cases, the material is vaporized to completion while in others the vaporization is stopped when a specific amount of material has been deposited. Resistive heating is the most common technique for vaporizing material at temperatures below about 1500°C, while focused electron beams are most commonly used for temperatures above 1500°C. Suggested vaporization sources for a variety of materials has been tabulated by a number of suppliers of source material and in publications.[16]

Resistively Heated Sources

The most common way of heating materials that vaporize below about 1500°C is by contact to a hot surface that is heated by passing a current through a material (resistively heated).[16]–[19] Evaporation sources must contain molten liquid without extensive reaction; the molten liquid must be prevented from falling from the heated surface. This is accomplished either by using a container such as a crucible, or by having a wetted surface.[20] The heated surface can be in the form of a wire, usually stranded, boat, basket, etc. Figure 5-6 shows some resistively heated source configurations.

Typical resistive heater materials are W, Ta, Mo, C, and BN/TiB_2 composite ceramics. Resistive heating of electrically conductive sources is typically by low voltage (<10 volts)—very high current (>several hundreds of amperes) AC transformer supplies. It is generally better to slowly increase the heater current than to suddenly turn on full heater power. Due to the low voltages used in resistive heating, contact resistance in the fixture is an important factor in source design. As the temperature increases, thermal expansion causes the evaporator parts to move; this movement should be accounted for in the design of the heater fixturing. Since metals expand on heating, the contacting clamps between the fixture and the source may have to be water cooled to provide consistent clamping and contact resistance.[21] The resistively-heated vaporization sources are typically operated near ground potential. If the sources are to be operated much above ground potential, filament isolation transformers must be used.

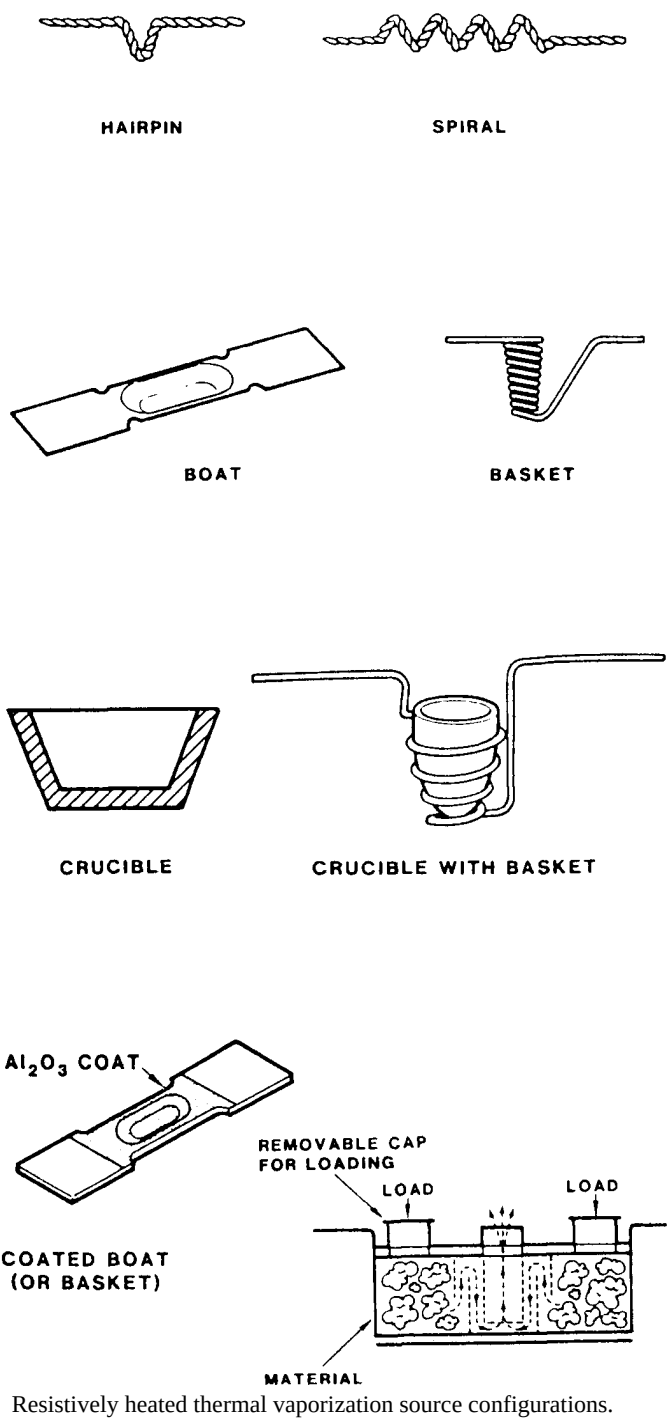


Figure 5-6. Resistively heated thermal vaporization source configurations.

Wetting is desirable to obtain good thermal contact between the hot surface and the material being vaporized.* The surface oxides on materials such as tungsten and tantalum will vaporize at temperatures below the melting point of most metals, allowing the molten materials to wet the surface of the clean metal. Wetted sources are also useful for depositing downward, sideways, or from non-planar surfaces. Metallic stranded wire, coils, and baskets are relatively cheap and can be used in many applications. Wire sources are generally of twisted strands of wire since the surface morphology tends to help wick and retain the molten material on the surface. Wires for evaporation are typically of tungsten[22][23] but can be of molybdenum or tantalum. Wire meshes and porous metals through which the molten metal wet and wick by capillary action, can be used for large area vaporization sources.

When evaporating a large amount of material from a wire source, the molten material tends to flow to the low spots where it may "drip" off as molten droplets. To minimize this problem, the filament can have a number of low spots such as with a horizontal coil; or bends or "kinks" can be put in the wire at selected points to collect the molten material at these points. Another way to retain the molten material in specific spots is to wrap a coil of tantalum wire around the tungsten heater at those spots, and that will help retain the molten material in that area.

Premelting and wetting of the evaporant on the heater surface prior to the beginning of the deposition has several benefits:

- Good thermal contact can be established
- Volatilization of volatile impurities and contaminants from the evaporant and from the surface of the heater

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*A technician had the problem that sometimes he could not get molten aluminum to wet the stranded tungsten filament in a vacuum deposition process. Questioning showed that he was obtaining the aluminum clips and tungsten filaments from reliable sources, he was cleaning the tungsten and the aluminum before use and that he was using a cryopumped system with a mechanical roughing pump. Further questioning elicited that the crossover from roughing to high vacuum pumping was at about 10 microns. This was well within the molecular flow range of his roughing system plumbing allowing backstreaming from the oil-sealed mechanical pump into the deposition chamber. The problem was that on heating the tungsten filament, the hydrocarbon oil on the filament "cracked" forming a carbon layer which the molten aluminum would not wet. The system was cleaned and the crossover pressure was raised to 100 mTorr and the problem went away.

- Overheating of the heater surface is avoided, thereby minimizing "spitting" and radiant heating from the source

Premelting can be done external to the deposition system if care is used in handling the source after premelting to prevent surface contamination. Premelting can be done in the evaporator system by using a shutter to prevent the deposition of undesirable material on the substrate before film deposition begins.

Radiation shields can be used to surround the hot vaporization source to reduce radiant heat loss. Generally radiation shields consist of several layers of refractory metal sheet separated from each other and the heated surface. These radiation shields:

- Reduce the power requirements of the source
- Reduce radiant heating from the source
- Allow the source to reach a higher temperature
- Have a more uniform temperature over a larger volume

Source fixturing involves making good electrical contact to the resistively heated vaporization source (wire, sheet, etc.). Thermal expansion requires that the fixture be somewhat flexible. If the fixture is rigid, the vaporization source can be stressed and break. If the source is flexible, such as a wire or coil, the source can distort, producing changes in the flux distribution pattern on heating and with use. In some cases, the source and its electrical connections are moved during deposition to increase coverage uniformity over a large stationary substrate.

High current connections to the source should be of a high conductivity material such as copper. Physical contact to boats and crucibles can be improved by using spring contacts of a material such as tungsten and graphite paper, such as Grafoil™ shimming materials. In some cases, cooled clamps can be used to hold the source. Multiple evaporation sources can be arranged to produce large area or linear vaporization patterns.[19]

Source degradation can occur with time. This can be due to reaction of the evaporant material with the heated surface. When there is reaction between the molten source material and the heater material, the vaporization should be done rapidly. For example, palladium, platinum, iron, and titanium should be evaporated rapidly from tungsten heaters. When using tungsten as the heater material, crystallization at high temperatures makes the tungsten brittle and causes microcracks, which create local hot spots that result in burn-out. On burn-out, some of the tungsten is vaporized and can contaminate the film. Generally it is better to replace

tungsten wire heaters after each deposition if such contamination poses a problem. When large masses of material that have wet the surface are allowed to cool in brittle containers (crucibles or boats), the stresses can crack the container material.

Electron Beam Heated Sources

Focused high energy electron beams are necessary for the evaporation of refractory materials, such as most ceramics, glasses, carbon, and refractory metals. This "e-beam" heating is also useful for evaporating large quantities of materials.[25]–[28] Figure 5-7 shows several sources using electron beam heating. When vaporizing solid surfaces of electrically insulating materials, local surface charge buildup can occur on the source surface leading to surface arcing that can produce particulate contamination in the deposition system.

In the deflected electron gun, the high energy electron beam is formed using a thermionic-emitting filament to generate the electrons, high voltages (10–20 kV) to accelerate the electrons, and electric or magnetic fields to focus and deflect the beam onto the surface of the material to be evaporated.[28]–[30] Electron beam guns for evaporation typically operate at 10–50 kW. Using high-power e-beam sources, deposition rates as high as 50 microns per second have been attained[31] from sources capable of vaporizing material at rates of up to 10–15 kilograms of aluminum per hour. Electron beam evaporators can be made compatible with UltraHigh Vacuum (UHV) processing.[32] Generally e-beam evaporators are designed to deposit material in the vertical direction, but high rate e-beam sources have been designed to deposit in a horizontal direction.[33]

In many designs, the electron beam is magnetically deflected through >180° to avoid deposition of evaporated material on the filament insulators. The beam is focused onto the source material which is contained in a water-cooled copper hearth "pocket." The electron beam can be rastered over the surface to produce heating over a large area. Electron gun sources can have multiple pockets so that several materials can be evaporated by moving the beam or the crucible, so that more than one material can be vaporized with the same electron source.

The high energy electron bombardment produces secondary electrons which are magnetically deflected to ground. The electrons ionize a portion of the vaporized material and these ions can be used to monitor the

evaporation rate. The ions can also create an electrostatic charge on electrically insulating substrates.[34][35] If the fixture is grounded, the electrostatic charge can vary over the substrate surface, particularly if the surface is large, affecting the deposition pattern. This variation can be eliminated by deflecting the ions away from the substrates by using a plate at a positive charge above the source or by electrically floating the fixture so that it assumes a uniform potential. E-beam deposition of dielectric materials can generate insulating surfaces, that can build-up a charge that causes arcing and particulate formation in the deposition system. With the e-beam evaporation of some materials, such as beryllium, significant numbers of ions are produced and they can be accelerated to the substrate, cause self-sputtering, and be used to modify the film microstructure.[36] The high-energy electron bombardment of the source material can produce soft x-rays which can be detrimental to sensitive semiconductor devices.[37]–[39]

The long-focus gun uses electron optics to focus the electron beam on a surface which can be an appreciable distance from the electron emitter.[40] The optic axis is often a straight line from the emitter to the evaporant and therefore the gun must be mounted off-axis from the source-substrate axis.

High voltage electron beam guns are not generally used in a plasma environment because of sputter erosion of the gun-filament by positive ions. There are also problems with the reaction of the hot filaments in reactive gases. In order to use an electron beam evaporator in a plasma or reactive gas environment, the electron emitter region can be differentially pumped by being isolated from the deposition environment. This is done by having a septum between the differentially-pumped electron emitter chamber and the deposition chamber; the septum has a small orifice for the electron beam to pass from one chamber to the other.[41] This type of configuration is used in e-beam ion plating.

Unfocused high-energy electron beam heating can be accomplished with an electron source by applying a voltage between the electron emitter and the source material or source container which is usually at ground potential. Such a source is referred to as a work-accelerated gun.[42][43]

High current, low energy electron beams or anodic arc vaporization source (Sec. 7.3.2) can be produced by thermoelectron emitting surfaces such as hollow cathodes.[44]–[49] They can be accelerated to several hundred volts and magnetically deflected onto the source which is at ground potential. Low energy electron beams are typically not very well focused but can have high current densities. The vaporization of a surface by the low energy electron beam can provide appreciable ionization of the

vaporized material since the vaporized atoms pass through a high-density low-energy electron cloud as they leave the surface. These "film ions" can be used in ion plating. Magnetic confinement of the electrons along the emitter-source axis can also be used to increase the electron path length so as to increase the ionization probability.[50][51]

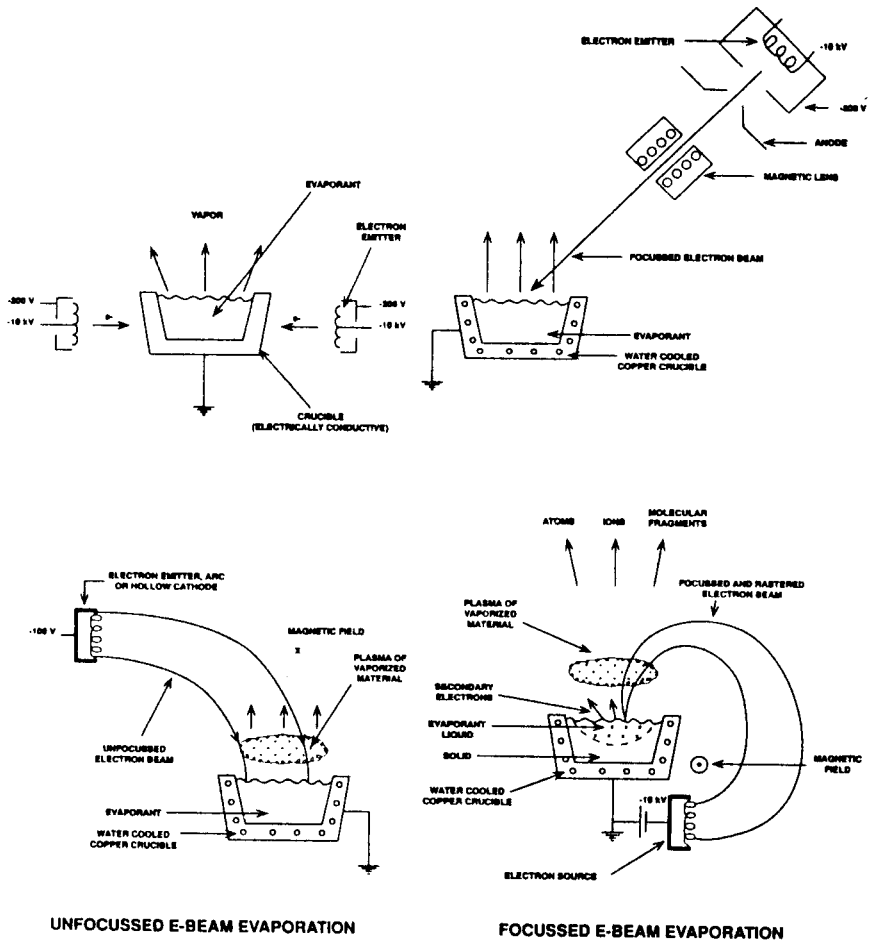


Figure 5-7. Electron beam (e-beam) vaporization sources.

Crucibles

Crucible containers can hold large amounts of molten evaporant but the vapor flux distribution changes as the level of the molten material changes. Electrically conductive containers can be heated resistively and can be in the form of boats, canoes, dimpled surfaces, crucibles,[52] etc. Typical refractory metals used for containers are tungsten, molybdenum, and tantalum as well as refractory metal alloys such as TZM (titanium and zirconium alloyed with molybdenum for improved high temperature strength) and tungsten with 5–20% rhenium to improved ductility. Metallic containers are often wetted by the molten material and the material can spread to areas where it is not desired. This spreading can be prevented by having non-wetting areas on the surface. Such non-wetting areas can be formed by plasma spraying Al_2O_3 or firing a glass frit on the surface.

Water-cooled copper is used as a crucible material when the evaporant materials are heated directly, as with electron beam heating. The design of the coolant flow is important in high rate evaporation from a copper crucible since a great deal of heat must be dissipated.[53] The water-cooled copper solidifies the molten material near the interface forming a "skull" of the evaporant material so that the molten material is actually contained in a like-material. This avoids reaction of the evaporant with the crucible material. On cooling, the evaporant "slug" shrinks and can be easily removed from the "pocket" of the electron beam evaporator. When using electron beam evaporation, care should be taken that the beam does not heat the crucible since the e-beam can vaporize the crucible materials as well as the evaporant material.

In some cases a liner can be used with a water cooled crucible. Examples of liner materials are: pyrolytic graphite, pyrolytic boron nitride, BN/TiB_2, BeO, Al_2O_3 and other such materials. Generally the liner materials have a poor thermal conductivity. This, along with the poor thermal contact that the liner, makes with the copper, allows the evaporant charge to be heated to a higher temperature than if the charge is in contact with the cold copper crucible. Liners can be fabricated in special shapes to attain desired characteristics.[54]

Electrically conductive ceramics can be used as crucibles. Carbon (graphite) and glassy carbon are commonly used crucible materials and when evaporating a carbon-reactive material from such a container, a carbide layer (skull) forms that limits the reaction with the container. For example, titanium in a carbon crucible forms a TiC "skull." When

evaporating a non-reactive material such as gold, graphite crucibles tend to form a powder that floats on the surface of the molten pool but does not evaporate. An electrically conductive composite ceramic that is used for evaporating aluminum is 50%-BN:50%-TiB_2 composite ceramic (UCAR™)[55] and TiB_2:BN:AlN composite ceramic.[56] These composite ceramics are stable in contact with molten aluminum, whereas most metals react rapidly with the molten aluminum at the vaporization temperature.

Glasses and electrically insulating ceramics can be used as crucibles and are often desirable because of their chemical inertness with many molten materials. Typical crucible ceramics are ThO_2, BeO, stabilized ZrO_2 (additions of HfO_2 & CaO to ZrO_2), Al_2O_3, MgO, BN, and fused silica. Kohl has written an extensive review of the oxide and nitride materials that may be of interest as crucible materials.[57] The ceramics can be heated by conduction or radiation from a hot surface though these are very inefficient methods of heating. For more efficient heating, the material contained in the electrically insulating crucible can be heated directly by electron bombardment of the surface or by rf inductive heating from a surrounding coil. Isotopic BN is a good crucible material for containing molten aluminum for rf heating. Metal sources such as boats, can be coated with a ceramic (e.g., plasma sprayed Al_2O_3) in order to form a ceramic surface in contact with the molten material.

Radio Frequency (rf) Heated Sources

Radio frequency (rf) sources are ones where rf energy is directly inductively coupled into an electrical conductor such as metals or carbon.[58] The rf can be used to heat the source material directly, or to heat the container ("susceptor") that holds the source material. This technique has been particularly useful in evaporating aluminum from BN and BN/TiB_2 crucibles.[59] When heating the source material directly, the containing crucible can be cooled.

Sublimation Sources

Sublimation sources have the advantage that the vaporizing material does not melt and flow. Examples of vaporization from a solid are: sublimation from a chunk of pure material, such as chromium, and sublimation from a solid composed of a subliming phase and a non-vaporizing phase, e.g., Ag:50%Li for lithium vapor and Ta:25%Ti alloy wire

(KEMET™) for titanium vapor. Heating can be by resistive heating, direct contact with a hot surface, radiant heating from a hot surface or bombardment by electrons.

A problem with sublimation of a solid material in contact with a heated surface is the poor thermal contact with the surface. This is particularly true if the evaporant can "jump-around" due to system vibration during heating. Often changing the source design such as changing from a boat to a basket source, eliminating mechanical vibration, using mesh "caps" on open-top sources, etc. can alleviate the problem. Direct electron beam heating of the material is generally more desirable for heating a subliming material than is contact heating.

Better thermal contact between the subliming material and the heater can be obtained by forming the material in physical contact with the heater by sintering powders around the heater or by electroplating the material onto the heater surface. Sintering generally produces a porous material that has appreciable outgassing. Chromium is often electrodeposited onto a tungsten heater. Electroplated chromium has an appreciable amount of trapped hydrogen and such a source should be heated slowly to allow outgassing of the material before chromium vaporization commences.

5.3.2 Replenishing (Feeding) Sources

Feeding sources are sources where additional evaporant material is added to the molten pool without opening the processing chamber. This is an important factor in performing long deposition runs such as are used for web coating. The feed-rate can be controlled by monitoring the level of the surface of the molten pool.[60] Feeding sources can use pellets,[61] powder, wires, tapes, or rods of the evaporant material. Pellet and powder feeding is often done with vibratory feeders, while wires and tapes are fed by friction and gear drives. Multiple wire-fed electron beam evaporators are often aligned to give a line source for deposition in a web coater.[62][63] Rod feeds are often used with electron beam evaporators where the end of the rod, whose side is cooled by radiation to a cold surface, acts as the crucible to hold the molten material. Feeding sources are used to keep the liquid level constant in a crucible, so as to retain a constant vapor flux distribution from the source and to allow vaporization of large amounts of material.

5.3.3 Baffle Sources

Some elements vaporize as clusters of atoms and some compounds vaporize as clusters of molecules. Baffle sources are designed so that the vaporized material must undergo several evaporations from heated surfaces before they leave the source to ensure that the clusters are decomposed. Baffle sources are desirable when evaporating silicon monoxide or magnesium fluoride for optical coatings to ensure the vaporization of mono-molecular SiO or MgF_2. Drumheller made one of the first baffle sources, called a "chimney source," for the vaporization of SiO.[64] Baffle sources can also be used to allow deposition downward or sidewise from a molten material.[65]

5.3.4 Beam and Confined Vapor Sources

Focused evaporation sources can be used to confine the vapor flux to a beam. Focusing can be done using wetted curved surfaces or by using defining apertures. A "beam-type" evaporation source using apertures has been developed to allow the efficient deposition of gold on a small area.[66] This source forms a $2\,^1/_2{}^o$ beam of gold giving a deposition rate of 40 Å per sec. at 5 cm.

A confined vapor source is one where the vapor is confined in a heated cavity and the substrate is passed through the vapor. The vapor that is not deposited stays in the cavity. Such a source uses material very efficiently and can produce very high rates of deposition. For example, a wire can be coated by having a heated cavity source such that the wire is passed through a hole in the bottom and out through a hole in the top. By having a raised stem in the bottom of the crucible, the molten material can be confined in a donut-shaped melt away from the moving wire. The wire can be heated by passing a current through the wire as it moves through the crucible.

5.3.5 Flash Evaporation

A constant-composition alloy film can be deposited using flash evaporation techniques where a small amount of the alloy material is periodically completely vaporized.[67]–[71] This technique is used to vaporize alloys whose constituents have widely differing vapor pressures. Flash evaporation can be done using a very hot surface and dropping a pellet or

periodically touching a wire tip to the surface so that the pellet or tip is completely vaporized.

Flash evaporation can be done by "exploding wire" techniques where very high currents are pulsed through a small wire by the discharge of a capacitor.[72] The majority of the vaporized material is in the form of molten globules. This technique has the interesting feature that the wire can be placed through a small hole and the vaporized material used to coat the inside of the hole.

Flash evaporation can also be done with pulsed laser vaporization of surfaces.[73]–[76] This technique is sometimes called Laser Ablation Deposition (LAD) or Pulsed Laser Deposition (PLD). Typically an excimer laser (YAG or ArF) is used to deposit energy in pulses. The YAG lasers typically deliver pulses (5ns, 5Hz) with an energy of about 1 J/pulse and the ArF lasers typically deliver pulses (20ns, 50Hz) with about 300 nJ/pulse. The vaporized material forms a plume above the surface where some of the laser energy is adsorbed and ionization and excitation occurs. In laser vaporization, the ejected material is highly directed; this makes it difficult to deposit a film with uniform thickness over large areas. During vaporization, molten globules are ejected, and these can be eliminated by using a velocity filter. Laser vaporization, combined with the passage of a high electrical current along the laser-ionization path to give heating and ionization, has been used to deposit hydrogen-free diamond-like carbon (DLC) films at an ablation energy density greater than 5×10^{10} W/cm^2. Laser vaporization with concurrent ion bombardment has been used to deposit a number of materials[77][78] including high quality high-temperature superconductor oxide films[79] at low substrate temperatures. Laser vaporization can be used to vaporize material from a film on a transparent material onto a substrate facing the film, by shining the laser through the "backside" of the transparent material, vaporizing a controlled film area and thus depositing a pattern directly on the substrate.[80]

5.3.6 Radiant Heating

The radiant energy E from a hot surface is given by $E = \partial T^4 A$, where ∂ is the emittance of the surface, T is the absolute temperature (Kelvin) and A is the area of emitting surface. Radiant energy from the hot vaporization source, heats all of the surfaces in the deposition chamber leading to a rise in the substrate temperature, desorption of gases from

surfaces, and surface creep of contaminants. Radiant heating of the substrate and interior surfaces can be minimized by:

- Using small heated areas (i.e., small *A* in the equation)
- Using pre-wetted evaporant surfaces
- Using radiation shields
- Using shutters over the source until the vaporization rate is established
- Rapid vaporization of the source material onto the substrate

5.4 TRANSPORT OF VAPORIZED MATERIAL

In the vacuum environment, the vapor travels from the source to the substrate in a straight line (line-of-sight) with collision with residual gas molecules (long mean free path).

5.4.1 Masks

Physical masks can be used to intercept the flux, producing defined patterns of deposition on a surface. The effectiveness of masks depends on the mask-surface contact, mask thickness, edge effects and mask alignment on the surface. Masks can be made in a number of ways such as etching or machining and can allow pattern resolutions as small as several microns. Masking allows the patterning of hard-to-etch materials and *in-situ* patterning during deposition. Deposited masks are used in the "lift-off" patterning process.[81] Programmed "moving masks" can also be used to control the film thickness distribution on a surface.[82][83]

5.4.2 Gas Scattering

Attempts to use higher gas pressure to give gas scattering ("scatter plating," "pressure plating," "gas plating") to randomize the flux distribution and improve the surface covering ability of evaporated films[84] has been singularly unsuccessful because of vapor phase nucleation (Sec. 5.12) and the low density of the deposited material.

5.5 CONDENSATION OF VAPORIZED MATERIAL

Thermally vaporized atoms may not always condense when they impinge on a surface; instead they can be reflected or re-evaporate. Re-evaporation is a function of the surface temperature and the flux of depositing atoms. A hot surface can act as a mirror for atoms. For example, the deposition of cadmium on a steel surface having a temperature greater than 200°C results in total re-evaporation of the cadmium. By placing hot mirrors around a three-dimensional substrate, cadmium can be deposited out of the line-of-sight of the thermal vaporization source.

5.5.1 Condensation Energy

When a thermally vaporized atom condenses on a surface, it gives up energy including:

- *Heat of vaporization or sublimation* (enthalpy change on vaporization)—a few eV per atom which includes the kinetic energy of the particle which is typically 0.3 eV or less
- *Energy to cool to ambient*—depends on heat capacity and temperature change
- *Energy associated with chemical reaction* (heat of reaction) which can be exothermic, when heat is released or endothermic, when heat is adsorbed
- Energy released on solution (alloying) or *heat of solution*

The heat of vaporization for gold is about 3 eV per atom, and the mean kinetic energy of the vaporized gold atom is about 0.3 eV, showing that the kinetic energy is only a small part of the energy released at the substrate during deposition. However it has been shown, using mechanical velocity filters, that the kinetic energy of the depositing gold atoms is important to the film structure, properties and annealing behavior.[85] At high deposition rates, the condensation energy can produce appreciable substrate heating.[86]

Deposition rates for vacuum deposition processes can vary greatly. They can range from less than one Monolayer per Second (MLS) (<3 Å/s) to more than 10^4 MLS (>3 microns/s). The rate depends on the thermal

power input to the source, system geometry, and the material. Generally the power input to the source is controlled by monitoring the deposition rate.

As shown in Fig. 5-4, the deposition thickness uniformity from a vaporizing point onto a plane is poor. A more uniform deposit over a planar surface can be obtained by using multiple sources with overlapping patterns; however this produces source control and flux distribution problems.[8] By moving the substrate further away, the uniformity over a given area can be improved; however the deposition rate is decreased as $1/r^2$. The most common technique to improve uniformity is to move the substrate in a random manner over the vapor source(s) using various fixture geometries (Sec. 3.5.5). Since the vaporization rate can change during the deposition process, the movement should sample each position a number of times during the deposition. Often the substrates are rotated on a hemispherical fixture (calotte) with the evaporant source at the center of the sphere to give a constant "*r*" in Eq. 2.

Since the deposition is line-of-sight, deposition on rough or non-planar surfaces can give geometrical shadowing effects resulting in non-uniform film thickness, surface coverage and variable film morphology (Sec. 9.4.2). This is particularly a problem at sharp steps and at oblique angles of deposition. Figure 5-8 shows the effect of angle-of-incidence on the depositing atom flux on covering a surface having a particle on the surface. These geometrical problems can be alleviated somewhat by extended vaporization sources, multiple sources, or substrate movement.

5.5.2 Deposition of Alloys and Mixtures

Alloys are mixtures of materials within the solubility limits of the materials. When the composition exceeds the solubility, the deposited materials are called mixtures. Atomically dispersed mixtures can be formed by PVD techniques since the material is deposited atom-by-atom on a cold surface. If the mixture is heated, then there will be phase separation. Alloys can be deposited directly by the vaporization of the alloy material if the vapor pressures of the constituents are nearly the same. However, if the vapor pressures differ appreciably, then the composition of the film will change as the deposition proceeds and the composition of the melt changes. In addition to depositing an alloy by vaporization of the alloy material directly, alloy films can be deposited using other techniques such as flash evaporation.

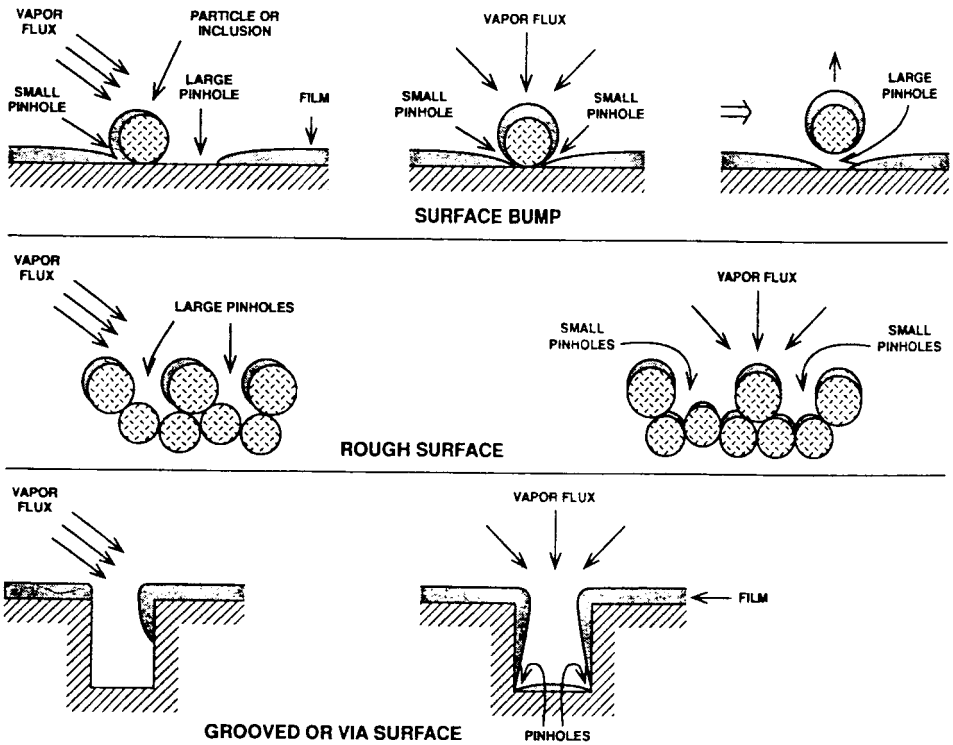


Figure 5-8. Geometrical shadowing of the deposition flux by a particle on the surface and by surface features.

One technique for depositing a constant composition alloy film is to use a rod-fed electron beam evaporation source where the temperature and volume of the molten pool is kept constant.[87]–[90] If the temperature and volume of a molten pool is kept constant and material is fed into the pool at the same rate as it is vaporized from the pool, the vapor will have the same composition as the incoming feedstock. Modern technology allows the deposition of alloys with a given composition if the constituents have partial pressures that do not vary by more than about 1000:1. For example, Ti-6-4 (titanium–6% aluminum–4% vanadium) can be evaporated from an electron beam heated rod-fed source to form alloy sheet and tape stock.

Alloy films can be formed by depositing alternating layers of the different materials from different sources. The layers are then diffused to form the alloy film. The alloy composition then depends on the relative amounts of materials in the films.

Alloy films can be deposited using multiple sources with individual deposition rate controllers. In this case the vapor flux distribution from each source must be taken into account. The multiple source technique can also be used to deposit layered composite films.[91] Multiple sources with overlapping flux distributions can be used to form films having a range of compositions over the substrate surface.

When depositing layered structures, the interface between the layers can be graded in composition from one composition to the other. This compositional grading can be accomplished by beginning the second deposition before the first is completed. This forms a "pseudo-diffusion" type interface (Sec. 9.3.4) between the two layers and prevents possible contamination/reaction of the first layer by the ambient environment before the second layer begins depositing. Grading the interface between deposited films provides better adhesion than when the interface abruptly changes from one material to the other.

5.5.3 Deposition of Compounds from Compound Source Material

When compound materials are vaporized, some of the lighter fragments, such as oxygen, are lost by scattering in the gas phase, and by not reacting with the deposited material when it reaches the substrate. For example, the vaporization of SiO_2 results in an oxygen-deficient (SiO_{2-x}) film that is yellowish in color. The composition of the deposited material

is determined by the degree of dissociation, the loss of materials in the mass transport process and by the reaction coefficient of the reactive species at the film surface. Sometime the lost oxygen can be replaced by quasi-reactive deposition in an oxygen ambient (Sec. 9.5), or postdeposition heat treatments in oxygen.[92]

The degree of reaction can be increased by bombardment and reaction of ions of reactive species from an reactive gas ion source. This process can be called Oxygen-Ion Assisted Deposition (IAD) if oxygen is the reactive gas.[93] For example SiO, which is easily thermally evaporated can be bombarded with oxygen ions to give $SiO_{1.8}$ which is of interest as a transparent, insulating, permeation-barrier coating on polymers for the packaging industry.[94]–[96]

Compounds can be formed by co-depositing materials and then having them react with each other. For example, titanium and carbon can be co-deposited to form a mixture, and when heated, TiC can be formed.

5.5.4 Some Properties of Vacuum Deposited Thin Films

Often vacuum deposited thin films have a residual tensile stress; seldom is the stress compressive except when the deposition is done at high temperatures. Generally the films are less than fully dense. Vacuum deposited compounds generally lose some of the more volatile and/or the lighter mass constituent during the vaporization-condensation process.

5.6 MATERIALS FOR EVAPORATION

Material placed in the vaporization source is called a “charge” and can be in the form of powder, chunks, wire, slugs, etc.

5.6.1 Purity and Packaging

The desired purity of the source material depends on the application and the effect of purity on film properties and process reproducibility. It is possible to obtain some material with extremely high purity (>99.999%) though the cost goes up rapidly with purity. Very reactive metals should be nitrogen-packed in glass ampoules to prevent oxidation, and opened and

handled in an inert gas dry box where the reactive gas content is kept low by the use of getter materials such as liquid NaK—K:Na (20–50%).

Purchase Specifications

Careful specification of purity, unallowable impurities, fabrication method, post-fabrication treatments, packaging, etc. of the source materials purchased can be important to obtaining a reproducible process. Using inexpensive material or material of unknown origin often creates problems. Often impurities such as O, N, C, and H are not specified by the supplier and they can be present in significant quantities. Examples of unspecified impurities are: oxidized surfaces of reactive metals, hydrogen incorporated in electrorefined chromium, carbon monoxide in nickel purified by the carbonyl process and helium in natural quartz. Generally it is better to specify vacuum-melted materials from the supplier when possible.

5.6.2 Handling of Source Materials

Source material should be carefully cleaned and handled since, on heating, the volatile impurities and surface contaminates are the first materials to be vaporized. In some cases, the evaporant materials should be cleaned before they are used. Materials should be handled with metallic instruments since abrasive transfer can contaminate surfaces in contact with polymers. The source and source material can be outgassed and premelted prior to film deposition.

5.7 VACUUM DEPOSITION CONFIGURATIONS

The primary function of the vacuum system associated with vacuum deposition processing is to reduce the level of contaminating residual gases and vapors to an acceptable level. Vacuum systems have been discussed in Ch. 3. Vacuum deposition poses no particular problems except for the high heat loads during thermal vaporization. Generally the vacuum chamber used for vacuum deposition is large, because the high radiant heat loads necessitate a large separation between the source and the substrate. In

some special cases such as web coating, the source-substrate distance may be short because the substrate is moving rapidly.

5.7.1 Deposition Chambers

Vacuum chambers are discussed in Sec. 3.5.2. Figure 5-9 shows the principal components of a batch-type vacuum deposition chamber. One important feature that is often found in vacuum deposition chambers is the relatively large distance between the heated source and the substrates. This is to minimize the radiate heating from the source and allows elaborate fixture motion to randomize the position of the substrates.

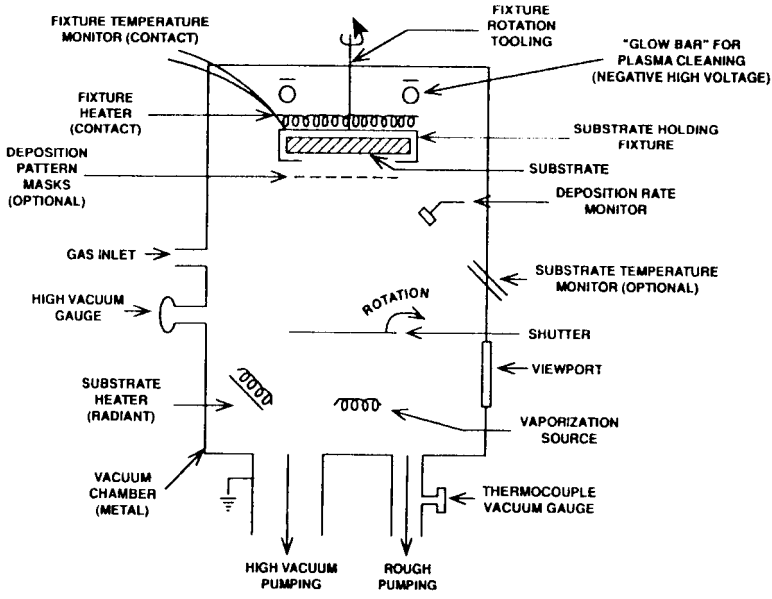


Figure 5-9. Components of a vacuum deposition chamber.

5.7.2 Fixtures and Tooling

Fixturing is used to hold the substrates while tooling is used to move the fixtures and were discussed in Sec. 3.5.5. Tooling is used to randomize the substrate position and angle with respect to the direction of

the depositing flux. A common tooling in vacuum deposition is a spherical dome-shaped (calotte) holder that maintains a constant line-of-sight distance between the source and substrates. Often this holder is rotated to randomize the position of the substrates. This results in improved surface coverage, a more uniform thickness distribution and more consistent film properties.[97]–[99] However, it should be realized that no amount of movement can completely overcome the angle-of-incidence and thickness variation on a complex surface though computer modeling can aid in determining the optimum conditions.[100] Fixture surfaces often represent a major portion of the surface in the processing chamber and should be cleaned, handled and stored with care.

Often material utilization in an evaporation process is poor unless proper fixturing and tooling is used to intercept the maximum amount of the flux. This can be accomplished by having the substrates as close as possible to the vaporization source, though this can result in excessive heating of the substrate during deposition. Deposition on large numbers of parts or over large areas can be done using large chambers with many (or large) vaporization sources.

Substrate mounting should be such that particles in the deposition ambient do not settle on the substrate surface. This means mounting the substrates so that they face downward or to the side. Mechanical clamping is often used to hold the substrates but this entails having a region that is not coated. Mechanical clamping provides poor and variable thermal and electrical contact to the fixture surface and can result in variable substrate temperatures during the vaporization/deposition process. Gravity can be used to hold the substrates as they are lying on a pallet fixture (facedown or up) or are held nearly vertically. Again these mounting techniques can give variable thermal and electrical contact to the surface. In some cases, the evaporation source can be moved and the substrate remain stationary. This is particulary useful if the substrate is large.

5.7.3 Shutters

Since the particles from a vapor source travel in straight lines in a vacuum, a moveable shutter can be used to intercept vaporized material and prevent it from reaching the substrate. The shutter is an important part of the vacuum deposition system. Shutters can be used to isolate the substrate from the source and allow outgassing and wetting of the source material without contaminating the substrate. The shutter can be closed

while a uniform deposition rate is established, and opening and closing the shutter can be used to define the deposition time.

Shutter design is limited only by the ingenuity of the designer. The shutter can be the moving part or the shutter can be fixed and the substrate moved. Shutters can be in the form of fans, leaves, flaps, sections of geometrical shapes such as cones, cylinders, etc. In designing a shutter, care must be taken to keep the complexity to a minimum. Shutter design should allow for easy removal for cleaning. In some cases, it may be desirable to cool the shutter to aid in retaining condensables.

5.7.4 Substrate Heating and Cooling

Often it is desirable to heat the substrates before deposition begins. This can be done by having the substrates in contact with a heated fixture. If the fixture is stationary an electrical heater can be used but if the fixture is being moved this can be difficult. Radiant heating from a hot source such as a tungsten-quartz lamp can often be used to heat surfaces in the vacuum system. Some materials such as SiO_2 do not adsorb infrared radiation very well and are not easily heated by radiation. Accelerated electrons have also been used to heat fixtures and lasers have been used to provide local heating. Some film materials, such as gold, are good heat reflectors and as soon as a gold film is formed, a high percentage of the incident radiant heat is reflected from the coated surface.

Substrate cooling is often a problem since cooling by convection is not operational in a vacuum. Substrates can be cooled by being in contact with a cooled substrate fixture. Circulating chilled water or oil, cooled water/ethylene glycol mixture (-25°C), dry ice/acetone (-78°C), refrigerants (≈ -150°C), or liquid nitrogen (-196°C) can be used as coolants in the substrate fixturing.

5.7.5 Liners and Shields

Liners and shields are discussed in Sec. 3.5.7. Vacuum deposition, because of the large spacing between source and substrate, often has a great deal of material deposited on non-removable surfaces and the use of liners and shields is particularly important.

5.7.6 *In Situ* Cleaning

In situ cleaning can be used in vacuum deposition systems. Many vacuum deposition systems, particularly optical coating systems, are equipped with the capability for establishing a plasma discharge that is used for cleaning substrate surfaces prior to film deposition (Sec. 12.10). A "plasma ring" or "glow bar" is used as the cathode in the processing chamber. The effectiveness of plasma cleaning depends on the packing of surfaces in the volume and the location and area of the glow bar. If there is a large area of fixturing/substrates and close spacing of surfaces in the chamber, the effectiveness of plasma cleaning will vary throughout the volume.

5.7.7 Getter Pumping Configurations

When depositing reactive materials, the walls, fixturing and shields in the deposition system can be arranged so as to provide "getter pumping" by the excess deposited film material. For example, a cylindrical tube can surround the volume between the vaporization source and the fixture in such a manner that a contaminate gas molecule will likely strike the surface of the coated cylinder before it can reach the growing film surface. This getter pumping lowers the contamination level in the system and at the substrate.

5.8 PROCESS MONITORING AND CONTROL

The principal process variables in vacuum deposition are:

- Substrate temperature
- Deposition rate
- Vacuum environment—pressure, gas species (Ch. 3)
- Angle-of-incidence of depositing atom flux (Ch. 9)
- Substrate surface chemistry and morphology (Ch. 2)

5.8.1 Substrate Temperature Monitoring

The substrate loses heat by conduction and radiation, and monitoring substrate temperature is often difficult. Thermocouples embedded in the substrate fixture often give a poor indication of the substrate temperature since the substrate often has poor thermal contact to the fixture. In some cases, thermocouples can be embedded in or attached directly to the substrate material. Optical (infrared) pyrometers allow the determination of the temperature if the surface emissivity and adsorption in the optics is constant and known.[101] When they are not known, the IR pyrometer can be used to establish a reproducible temperature even if the value is not known accurately.

Soda-lime glass (common window glass), which is a glass material that is commonly used as a substrate material, has a high adsorption for infrared radiation so the IR pyrometer can look at the front surface of the glass while a radiant heater is heating it from the backside and the pyrometer will not see the IR from the heater. Passive temperature monitors can be used to determine the maximum temperature a substrate has reached in processing. Passive temperature monitors involve color changes, phase changes (e.g. melting of indium) or crystallization of amorphous materials.[102]

5.8.2 Deposition Monitors—Rate and Total Mass

The deposition rate is often an important processing variable in PVD processing. The rate can affect not only the film growth but it, along with the deposition time, is often used to determine the total amount of material deposited. The quartz crystal deposition rate monitor (QCM) is the most commonly used *in situ*, real-time deposition rate monitor for PVD processing.[103]–[105]

Single crystal quartz is a piezoelectric material, which mean that it responds to an applied voltage by changing volume which causes the surfaces to move. The amount of movement depends on the magnitude of the voltage. If the voltage is applied at a high frequency (5 MHz range) the movement will resonate with a frequency that depends on the crystalline orientation of the quartz crystal slab and its thickness. Quartz crystal deposition monitors measure the change in resonant frequency as mass (the film) is added to the crystal face. The change in frequency is directly proportional to the added mass. By calibrating the frequency change with mass deposited, the quartz crystal output can provide measurements of

the deposition rate and total mass deposited. The frequency change of the oscillation allows the detection of a change of mass of about 0.1 microgram/cm^2 which is equivalent to less than a monolayer of deposited film material.

The quartz crystal can be cut with several crystalline orientations. The most common orientation is the AT-cut which has a low temperature dependence of its resonant frequency near room temperature. Other cuts have a higher temperature dependence. Typical commercial quartz crystal deposition monitors have a crystal diameter of about one-half inch and a total probe diameter of about one inch. The crystal is coated on both faces to provide the electrodes for applying the voltage and is generally water cooled to avoid large temperature changes.

Ideally the QCM probe should be placed in a substrate position. Often this is impossible because of the size of the substrate, fixture movement, or system geometry, so the probe is placed at some position where it samples a part of the deposition flux. The probe readings are then calibrated to total film thickness deposited. As long as the system geometry and vaporization flux distribution stays constant, then the probe readings are calibrated within a deposition run and from run-to-run. The QCM probe can be shielded so as to sample the deposition flux from a small area so several monitors can be used to independently monitor deposition from several vaporization sources close to each other. The output from the monitors can be use to control the vaporization rates as well as the deposition time.

The major concerns with the use of QCMs are calibration with the actual deposition flux, probe placement, intrusion of the probe into the deposition chamber, temperature rise if the probe is not actively cooled, and calibration changes associated with residual film stress and film adhesion to the probe face. The total residual film stress, which changes with film thickness, can change the elastic properties of the quartz crystal and thus the frequency calibration. In some cases, the magnitude of the change can be more than the effect of mass change. The presence of film stress and its affect can be determined using two QCMs that have different crystalline orientations. Crystals with different orientations have different elastic properties. If there is no film stress then the probe readings should be the same during film deposition. If not, then film stress is probably a problem that has to be considered. Care must be taken in using this observation in that the stress in the film on the probe face may not be the same as the film stress present in films deposited on the substrates. Often QCM probes are used for several or many deposition runs. If the film

deposited on the probe has adsorbed gases or water vapor between runs then desorption of these gases and vapors during the deposition can affect the calibration.

Ionization deposition rate monitors are commercially available but are not commonly used. Ionization rate monitors compare the collected ionization currents in a reference ionizing chamber and an ionizing chamber through which the vapor flux is passing. By calibration, the differential in gauge outputs can be used as a deposition rate monitor.[106] In electron beam evaporation, the ions that are formed above the molten pool can be collected and used to monitor the vaporization rate.[107] The optical emission of the excited species above the vaporization source can be used for rate monitoring. Some deposition rate monitors use optical atomic adsorption spectrometry (AAS) of the vapor as a non-intrusive rate monitoring technique (Sec. 6.8.8).

In many cases, the total amount of deposited material is controlled by evaporating-to-completion of a specific amount of source material. This avoids the need for a deposition controller and is used where many repetitious depositions are made with a constant system geometry.

5.8.3 Vaporization Source Temperature Monitoring

Generally vaporization source temperatures are very difficult to monitor or control in a precise manner. Since the vaporization rate is very temperature-dependent, this makes controlling the deposition rate by controlling the source temperature very difficult. In Molecular Beam Epitaxy (MBE) the deposition rate is controlled by careful control of the temperature of a well-shielded Knudsen cell source using embedded thermocouples.[4][5]

5.8.4 *In Situ* Film Property Monitoring

There is no easy way to measure the geometrical thickness of a film during deposition since the thickness depends on the density for a given mass deposited. Generally thickness is determined from the mass that is deposited assuming a density so that the mass gauge is calibrated to provide thickness.

In optical coating systems, *in-situ* monitoring of the optical properties of the films is used to monitor film deposition and provide feedback to control the evaporators.[108][109] Generally the optical transmittance,

interference (constructive and destructive), or reflectance at a specific wavelength, is used to monitor the optical properties. Ellipsometric measurements can be used to monitor the growth of very thin films of electrically insulating and semiconductor materials using an *in situ* ellipsometer.[110] Optical extinction, X-ray attenuation, and magnetic eddy current[111] measurements are useful for making non-contacting measurements on moving webs in vacuum web coating.

There are several techniques for measuring the film stress during the deposition process.[110][112]–[115] Generally these techniques use the deflection of a beam (substrate) by optical interferometry or by an optical lever arm using a laser beam. *In situ* X-ray diffraction measurements of the lattice spacing can be used to measure film stress due to lattice deformation.[116]

An electrically conducting path between electrodes can be deposited using a mask and the electrical resistivity of the path can then be used as a deposition monitor.[117]

5.9 CONTAMINATION FROM THE VAPORIZATION SOURCE

5.9.1 Contamination from the Vaporization Source

When heating the source material, volatile species on the surface and in the bulk are the first to vaporize. This source of contamination can be controlled by proper specification and handling of the source material.

In the evaporation of materials from a heated surface, "spits" and "comets" are often encountered. Spits are solidified globules of the source material found in the deposited film. The spits form bumps in the deposited film and when these poorly bonded globules are disturbed, they fall out leaving large pinholes in the film. Comets are the bright molten droplets seen traversing the space between the source and the substrate. Molten globules originate from the molten material by several processes.

Spits can occur when melting and flowing a material on a hot surface. A solid material placed on a surface has poor thermal contact with the surface so the tendency is to heat the surface to a very high temperature. When the evaporant melts and spreads over the surface, the very hot surface creates vapor that "explodes" through the spreading molten material. This source of spits can be eliminated by premelting the charge on the

surface to give good thermal contact and by using shutters in the system so the substrate cannot see the source until the molten charge has wetted the surface and is vaporizing uniformly.

On heating, particularly rapid heating, gases and vapors in the molten source material can agglomerate into bubbles and explode through the surface giving spits. For example, silver can have a high content of dissolved oxygen and give spitting problems when heated. The source of spits can be continual if new material is continually being added to the melt. Spits can be reduced by using pure vacuum-melted source material, handled and stored in an appropriate way, and by degassing the evaporant charge by premelting, or by slow heating to melting.

If the molten evaporant is held in a heated crucible, vapor bubbles can form on the crucible surfaces where they grow and break loose. As the bubbles rise through the molten material, the hydrostatic pressure decreases and the bubbles grow in size. When the bubbles reach the surface they "explode" giving rise to globules of ejected molten material. Materials having high vapor pressures at their melting points are more likely to give spits than are materials which have a low vapor pressure at their melting point. Spitting is common when boiling water; in high school chemistry, students are taught to add "boiling beads" to the water to reduce the violence and splashing during rapid boiling. The same approach can be used to prevent spitting from molten material. For example, chunks of tantalum are placed in molten gold to prevent gold spits. The tantalum does not react with the gold and does not vaporize at the gold evaporation temperatures.

Spits from crucibles can be minimized by:

- Using source materials that are free of gases and high vapor pressure impurities
- Polishing the crucible surfaces so that bubbles do not stick well and break loose when they are small
- Using "boiling beads" in the molten material to prevent large bubbles from forming
- Using baffle-type sources such that the source material must be vaporized several times before the vapor leaves the source
- Using specially designed crucibles[64]
- Reducing the vaporization rate

Refractory metals (W, Ta, Mo) used for resistive heaters are covered with oxides which volatilize at temperatures lower than the vaporization temperature of many source materials. If film contamination by these oxides is to be avoided, the heater material should be cleaned before installation, shutters should be used, or the surface pre-wetted by the source material.

5.9.2 Contamination from the Deposition System

Radiant heating from the process can increase the desorption of species from vacuum surface and materials in the system. Particulates can also be formed in the vacuum deposition system due to wear and abrasion from the moving fixturing/tooling which is often used in vacuum deposition systems in order to randomize the position of the substrates. The formation of pinholes in films deposited on smooth surfaces is generally due to the presence of particulate contamination on the surface during deposition. By depositing a film onto a smooth glass surface, using tape to expose the pinholes and counting the pinholes, a measure of the particulate contamination in the system can be made.

5.9.3 Contamination from Substrates

Contamination can be brought-in with the substrates. Substrates should be prepared and handled as discussed in Ch. 12.

5.9.4 Contamination from Deposited Film Material

Film buildup on surfaces in the deposition chamber increases the surface area. This makes removing water vapor from the surfaces progressively more difficult with use. The film buildup can also flake-off giving particulate contamination in the deposition system.[118] Fixturing should be positioned such that particulates that are formed do not fall on the substrate surface.

5.10 ADVANTAGES AND DISADVANTAGES OF VACUUM DEPOSITION

Vacuum deposition has advantages and disadvantages compared to other PVD techniques.

Advantages in some cases:

- Line-of-sight deposition allows the use of masks to define area of deposition
- Large-area sources can be used for some materials (e.g., "hog trough" crucibles for Al and Zn)
- High deposition rates can be obtained
- Deposition rate monitoring is relatively easy
- Vaporization source material can be in many forms such as chunks, powder, wire, chips, etc
- Vaporization source material of high purity is relatively inexpensive
- High purity films are easily deposited from high purity source material since the deposition ambient can be made as non-contaminating as is desired
- Technique is relatively inexpensive compared to other PVD techniques

Disadvantages in some cases:

- Line-of-sight deposition gives poor surface coverage—need elaborate tooling and fixturing
- Line-of-sight deposition provides poor deposit uniformity over a large surface area without complex fixturing and tooling
- Poor ability to deposit many alloys and compounds
- High radiant heat loads during processing
- Poor utilization of vaporized material
- Non-optimal film properties—e.g., pinholes, less than bulk density, columnar morphology, high residual film stress
- Few processing variables available for film property control

5.11 SOME APPLICATIONS OF VACUUM DEPOSITION

Vacuum deposition is the most widely used of the PVD deposition processes. Applications of vacuum deposition include:

- Electrically conductive coatings—ceramic metallization (e.g., Ti-Au, Ti-Pd-Au, Al, Al-Cu-Si, Cr-Au, Ti-Ag), semiconductor metallization (e.g., Al : Cu (2%) on silicon), metallization of capacitor foils (e.g., Zn, Al)
- Optical coatings—reflective and anti-reflective multilayer coatings, heat mirrors, abrasion resistant topcoats
- Decorative coatings (e.g., Al, Au on plastics)
- Moisture and oxygen permeation barriers—packaging materials (e.g., Al and $SiO_{1.8}$ on polymer webs)
- Corrosion resistant coatings—(e.g., Al on steel)
- Insulating layers for microelectronics
- Selenium coatings for electrography or xerography
- Avoidance of many of the pollution problems associated with electroplating ("dry processing")
- Fabrication of free-standing structures
- Vacuum plating of high strength steels to avoid the hydrogen embrittlement associated with electroplating (e.g., Cd on steel—"vacuum cad plating")

5.11.1 Freestanding Structures

The properties of thick vacuum deposited alloy deposits were studied extensively in the 1960's.[119][120] The technology was developed to produce 0.002 inch thick titanium alloy foils by depositing on a moving drum then removing the foil from the drum.

Vacuum deposition processes can be used to form freestanding structures by depositing the film on an appropriately shaped mandrel. On the mandrel there is either a "parting layer," such as evaporated NaCl, or the surfaces may be non-adhering, such as copper on the oxide on stainless steel. In some cases, the mandrel must be dissolved to release the deposited form. This technique is used to fabricate thin-walled structures and windows.[121]

5.11.2 Graded Composition Structures

Since films formed by vacuum deposition are deposited atom-by-atom, films with a continuously changing (graded) composition can be deposited by co-deposition.

5.11.3 Multilayer Structures

Many applications of vacuum deposition require deposition of layered structures. These applications range from simple 2–3 layer metallization systems to X-ray diffraction gratings consisting of alternating low mass material (carbon) and high mass material (tungsten) to form a stack of thousands of layers with each layer only 30–40 angstroms thick.

5.11.4 Molecular Beam Epitaxy (MBE)

Probably the most sophisticated PVD process is Molecular Beam Epitaxy (MBE) or Vapor Phase Epitaxy (VPE).[122]–[124] MBE is used to form epitaxial films of semiconductor materials by carefully controlled vacuum deposition. In MBE, a vacuum environment of better than 10^{-9} Torr is used and the film material is deposited from a carefully rate-controlled vapor source (Knudsen-type source). The MBE deposition chamber can also contain a wide range of analytical instruments for *in situ* analysis of the growing film. These analytical techniques include methods for measuring crystal parameters such as Reflection High Energy Electron Diffraction (RHEED) and Low Energy Electron Diffraction (LEED).

Gaseous or vaporized metalorganic compounds can also be used as the source of film material in MBE. The molecular species are decomposed on the hot substrate surface to provide the film material. The use of metalorganic precursor chemicals is called Metal-Organic Molecular Beam Epitaxy (MOMBE).[125] MOMBE is used in low temperature formation of compound semiconductors with low defect concentrations.

5.12 GAS EVAPORATION AND ULTRAFINE PARTICLES

Gas evaporation is a term given to the production of ultrafine particles ("smokes") formed by gas phase nucleation due to collision of the evaporated atoms with residual gas molecules. This typically requires an ambient gas pressure greater than about 10 Torr. The formation of useful films of ultrafine particles formed by gas evaporation was reported by Pfund who produced "zinc black" infrared absorbing films in 1933.[126] Vapor phase nucleation can occur in a dense vapor cloud by multi-body collisions and the nucleation can be encouraged by passing the atoms to be nucleated through a gas to provide the necessary collisions and cooling for nucleation.[127]–[131] These particles have a size range of 10–1000 Å and the size and size distribution of the particles is dependent on the gas density, gas species, evaporation rate, and the geometry of the system.[132] When these particles deposit on a surface, the resulting film is very porous and can be used as a optical radiation trap, e.g., "black gold" infrared radiation bolometer films, germanium film solar absorber coatings,[133] low secondary electron emission surfaces,[134] and porous electrode films.[135] The particles themselves are used for various powder metallurgical processes, such as low-pressure, low-temperature sintering.[136]

Ultrafine particles of reactive materials are very pyrophoric because of their high surface area. Ultrafine particles of reactive materials such as titanium form an oxide layer on the surface when exposed to air. The particles with this oxide layer are stable, but if the oxide is disturbed the particles will catch on fire and a flame front will sweep over the surface.* To avoid this oxide in commercial fabrication of ultrafine particles, the particles are scraped from the surface and collected in a vacuum container before the system is opened.

Ultrafine particles of alloys can be formed by evaporation from a single source or evaporation from separate sources and nucleated in the gas. Ultrafine particles of compounds can be formed by having a reactive gas present during nucleation, or by decomposition and reaction of precursor gases in an arc or plasma. Formation of the ultrafine particles in a plasma

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*In the early work on ion plating, the particles formed in the plasma and deposited on the walls were called "black sooty crap" (BSC). One game was to ask an observer to wipe the particles off a window with a paper towel. When the window was wiped the towel caught on fire and a flame front moved over the interior surface of the chamber.

results in the ultrafine particles having a negative charge and are suspended in the plasma near walls where they can grow to appreciable size.[137]–[139]

Recently gas evaporation techniques have allowed the formation of the buckministerfullerenes (C^{60} and C^{70}—"buckey-balls"), a newly discovered form of the carbon molecule. The synthesis involves arcing two pure graphite electrodes in a partial vacuum containing helium. The carbon "soot" that forms contains from 3–40% fullerenes depending on the conditions. The fullerenes are extracted from the soot by dissolving the carbon in boiling benzene or tolulene followed by vacuum drying.

5.13 OTHER PROCESSES

5.13.1 Reactive Evaporation and Activated Reactive Evaporation (ARE)

Reactive evaporation is the formation of films of compound materials by the deposition of atoms in a partial pressure of reactive gas. Reactive evaporation was first reported by Auwarter in 1952 and Brinsmaid et al in 1953. Reactive evaporation does not produce dense films since the gas pressure required for reaction causes gas phase nucleation and deposition of ultrafine particles along with the vaporized materials.

In 1971 Heitmann used reactive evaporation to deposit oxide films by evaporating the film material through a low-pressure plasma containing oxygen and this technique is now generally called "Activated Reactive Evaporation (ARE)".[140] In activated reactive evaporation the reactive gas is "activated" and is made more chemically reactive so that ARE can be done at a lower gas pressure than reactive evaporation. When a surface is in contact with a plasma, it attains a negative potential with respect to the plasma. Thus gas-phase-nucleated particles attain a negative charge, as does the substrate in contact with the plasma, so the ultrafine particles do not deposit on the substrate. Often activated reactive evaporation is performed with a negative bias on the substrate and is sometimes called Bias Active Reactive Evaporation (BARE)[141] which is a type of Ion Plating process (Ch. 8).

Thermal evaporation for reactive deposition has the advantage that material can be deposited much faster than with sputtering or arc vaporization. This is a particular advantage in web coating and a great deal of work has been done on activated reactive evaporation for web coating.[142]–[145]

5.13.2 Jet Vapor Deposition Process

In the "jet vapor deposition" (JVD™) process, evaporated atoms/molecules are "seeded" into a supersonic jet flow of inert carrier gas that expands into a rapidly pumped vacuum chamber.[146]–[148] The jet transports the atoms/molecules to the substrate surface where they are deposited. The vapor source can be in the form of thermal evaporation or sputtering and is located in the jet nozzle. The deposition chamber pressure is about 1 Torr and is pumped using high capacity mechanical pumps. The JVD™ process can be combined with high-current ion bombardment for *in situ* control of the film properties.[149]

5.13.3 Field Evaporation

Surface atoms of metals can be vaporized by a high electric field. This technique is known as field evaporation and can be directly observed in the field ion microscope.[150] This vaporization technique is used to clean emitter tips in field ion microscopy and to form metal ions from liquid-metal-coated tips. Field evaporation has been used to directly deposit nanometer-size gold structures.[151] The very sharp tips necessary to obtain the high electric field can be formed in a variety of ways.[152]

5.14 SUMMARY

Vacuum deposition is the most energy efficient of the PVD processes. Where the substrate coverage, adhesion, process throughput, and film properties are acceptable, it is generally the PVD process of choice.

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6

Physical Sputtering and Sputter Deposition (Sputtering)

6.1 INTRODUCTION

The physical sputtering (sputtering) process, or pulvérisation as the French call it, involves the physical (not thermal) vaporization of atoms from a surface by momentum transfer from bombarding energetic atomic-sized particles. The energetic particles are usually ions of a gaseous material accelerated in an electric field.[0a] Sputtering was first observed by Grove in 1852 and Pulker in 1858 using von Guericke-type oil-sealed piston vacuum pumps. The terms "chemical sputtering" and "electro-chemical sputtering" have been associated with the process whereby bombardment of the target surface with a reactive species produces a volatile species.[1] This process is now often termed "reactive plasma etching" or "reactive ion etching" and is important in the patterning of thin films.[2]

Sputter deposition, which is often called just sputtering (a poor use of the term), is the deposition of particles whose origin is from a surface (target) being sputtered. Sputter deposition of films was first reported by Wright in 1877 and was feasible because only a relatively poor vacuum is needed for sputter deposition. Edison patented a sputter deposition process for depositing silver on wax photograph cylinders in 1904. Sputter deposition was not widely used in industry until the need developed for reproducible,

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stable long-lived vaporization sources for production and the advent of magnetron sputtering. Planar magnetron sputtering, which uses a magnetic field to confine the motion of secondary electrons to near the target surface, is presently the most widely used sputtering configuration and is derived from the development of the microwave klystron tube in WW II, the work of Kesaev and Pashkova (1959) in confining arcs and Chapin (1974) in developing the planar magnetron sputtering source. Early reviews of sputtering were published by Wehner,[3] Kay,[4] Maissel,[5] and Holland.[6]

Typically the use of the term sputter deposition only indicates that a surface being sputtered is the source of the deposited material. In some cases, the sputtering configuration may be indicated (e.g., ion beam sputtering, magnetron sputtering, unbalanced magnetron sputtering, rf sputtering, etc.). In some cases special sputtering conditions may be indicated such as reactive sputter deposition for the deposition of compound films or bias sputtering[7][8] when a bias is placed on the substrate so that there is concurrent ion bombardment of the depositing film (Ch. 8).

Sputter deposition can be done in:

- A good vacuum (< 10^{-5} Torr) using ion beams
- A low pressure gas environment where sputtered particles are transported from the target to the substrate without gas phase collisions (i.e., pressure less than about 5 mTorr) using a plasma as the ion source of ions
- A higher pressure gas where gas phase collisions and "thermalization" of the ejected particles occurs but the pressure is low enough that gas phase nucleation is not important (i.e., pressure greater than about 5 mTorr but less than about 50 mTorr).

Sputter deposition can be used to deposit films of compound materials either by sputtering from a compound target or by sputtering from an elemental target in a partial pressure of a reactive gas (i.e., "reactive sputter deposition"). In most cases, sputter deposition of a compound material from a compound target results in a loss of some of the more volatile material (e.g., oxygen from SiO_2) and this loss is often made-up by deposition in an ambient containing a partial pressure of the reactive gas and this process is called "quasi-reactive sputter deposition." In quasi-reactive sputter deposition, the partial pressure of reactive gas that is needed is less than that used for reactive sputter deposition.

6.2 PHYSICAL SPUTTERING

The momentum-transfer theory for physical sputtering was proposed early-on but was supplanted by the "hot-spot" theory involving thermal vaporization. It has only been in recent years that the true nature of the physical sputtering process has been defined and modeled. Much of that knowledge came from the work of Guntherschulze in the 1920's and 30's and Wehner and his co-workers in the 1950's and 60's, when a number of effects were demonstrated that could only be explained by a momentum transfer process. These effects include:

1. The sputtering yield (ratio of atoms sputtered to the number of high energy incident particles) depends on the mass of the bombarding particle as well as its energy.
2. The sputtering yield is sensitive to the angle-of-incidence of the bombarding particle.
3. There is a "threshold energy" below which sputtering does not occur no matter how high the bombarding flux.
4. Many sputtered atoms have kinetic energies much higher that than those of thermally evaporated atoms.
5. Atoms ejected from single crystals tend to be ejected along directions of the close packed planes in the crystal.[9]
6. In a polycrystalline material some crystallographic planes are sputtered faster than are others (preferential sputter etching).
7. Atoms sputtered from an alloy surface are deposited in the ratio of the bulk composition not their relative vapor pressures as is the case in thermal vaporization.
8. Sputtering yields decrease at very high energies because the ions lose much of their energy far below the surface.
9. The sputtering yield is rather insensitive to the temperature of the sputtering target.
10. There is no sputtering by electrons even at very high temperatures.
11. The secondary electron emission by ion bombardment is low. Whereas high rates from thermoelectron emission would be expected if high temperatures were present.

Effects 1 through 7 above are important to the growth of films by sputter deposition. This is particularly true for low-pressure (<5 mTorr) sputtering where the energetic sputtered atoms and reflected high energy neutrals are not "thermalized" by collision between the sputtering source (target) and the substrate.

There are still some questions about the details of the sputtering process since the surface region of the target is modified by the bombardment process. This modification includes incorporation of the bombarding species into the film,[10][11] preferential diffusion and the generation of lattice defects to the point of completely destroying the crystallographic structure ("amorphorization") of the surface region.[12]

6.2.1 Bombardment Effects on Surfaces

Figure 6-1 shows the processes that occur at the surface region and in the near-surface region of the bombarded surface. The bombarding particles can physically penetrate into the surface region while the collision effects can be felt into the near-surface region. The bombarding particle creates a collision cascade and some of the momentum is transferred to surface atoms which can be ejected (sputtered). Most of the transferred energy (>95%) appears as heat in the surface region and near-surface region. Some of the bombarding particles are reflected as high energy neutrals and some are implanted into the surface.[13][13a] The process of deliberately incorporating krypton into surfaces has been called krypyonation and the materials thus formed called kryptonates.[13b]–[13f] The release of radioactive krypton from the kryptonates has been used as a high-temperature thermal indicator.

When an atomic sized energetic particle impinges on a surface the particle bombardment effects can be classed as:

- Prompt effects ($<10^{-12}$ sec)—e.g., lattice collisions, physical sputtering, reflection from the surface
- Cooling effects ($>10^{-12}$ to $<10^{-10}$ sec)—e.g., thermal spikes along collision cascades
- Delayed effects ($>10^{-10}$ sec to years)—e.g. diffusion, strain-induced diffusion, segregation
- Persistent effects—e.g., gas incorporation, compressive stress due to recoil implantation

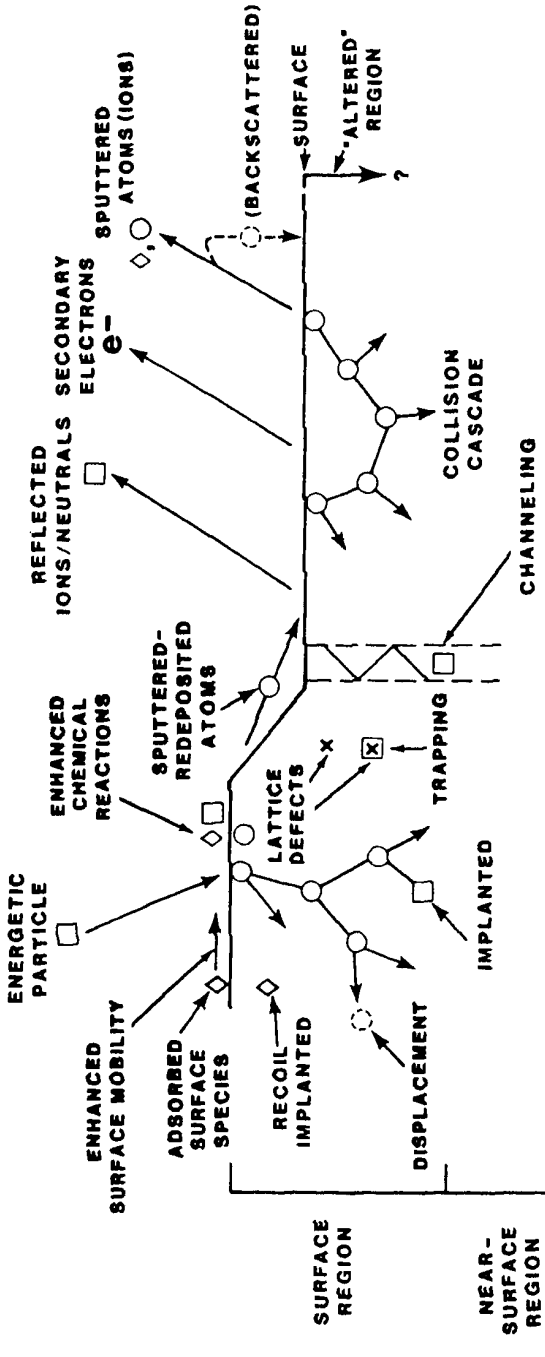


Figure 6-1. Events that occur on a surface being bombarded with energetic atomic-sized particles.

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When sputtering is performed in a low pressure or vacuum environment, high energy reflected neutrals of the bombarding gas and high energy sputtered atoms from the target bombard the growing film and affect the film formation process. High energy bombardment can cause resputtering of the depositing material giving an apparent decrease in the sputtering yield from the target.[14][15] The flux of reflected energetic neutrals may be anisotropic giving anisotropic properties in the resulting deposited film. For example, the residual film stress in post-cathode magnetron sputtered deposited films depends on the relative orientation of the film with respect to the post cathode orientation.[16] A major problem with energetic neutral bombardment of the growing film is that it is often not recognized and not controlled.

In sputtering, the sputtering target generally is actively cooled. The cold surface minimizes the amount of radiant heat in a sputtering system and is an advantage over thermal evaporation in vacuum where the radiant heat load can be appreciable. The low level of radiant heat is one factor that allows thermally-sensitive surfaces to be placed near the sputtering target. Cooling also prevents diffusion in the target which could lead to changes in the elemental composition in the surface region when alloy targets are used.

The surface region of the sputtering surface traps gas from the bombarding species. This "gas charging" produces a high chemical concentration gradient ("chemical potential") and can give rise to a high diffusion rate of the bombarding species into the target surface if the bombarding species is soluble in the target material. This is used to advantage in "plasma nitriding" or "ionitriding" process where ion bombardment cleans the surface and a moderate temperature allows diffusion of nitrogen into the material and reaction with some of the base material to form a thick reaction layer.

The mass of the bombarding species is important to the energy and momentum transferred to the film atom during the collision. From the Laws of Conservation of Energy and the Conservation of Momentum the energy, E_t, transferred by the physical collision between hard spheres is given by:

$$E_t/E_i = 4\, M_t M_i \cos^2 \theta/(M_i+M_t)^2$$

where E = energy, M = mass, i = incident particle, t = target particle and θ is the angle of incidence as measured from a line joining their centers of masses (as shown in Fig. 6-2).

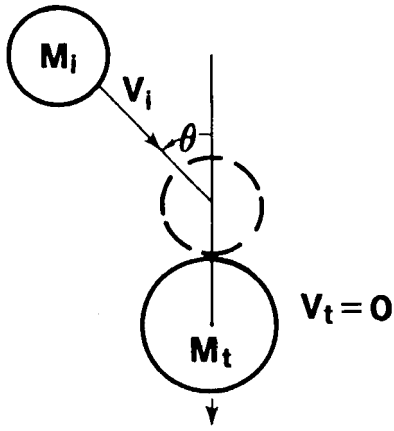


Figure 6-2. Collision of particles.

The maximum energy is transferred when $\cos\theta = 1$ (zero degrees) and $M_i = M_t$. Therefore matching the atomic mass of the bombarding ion to the target atom is important to the sputtering yield. This makes krypton (84 amu), xenon (131 amu) and mercury (201 amu) ions attractive for sputtering heavy elements, and light ions such as nitrogen (14 amu) unattractive. This advantage is typically outweighed by other considerations such as cost of the sputtering gas, health concerns or the desire to perform "reactive sputter deposition" of oxides and nitrides. It is interesting to note that much of the early work on sputtering was done using mercury ions.

Typically argon (40 amu) is used for inert gas sputtering since it is a relatively inexpensive inert gas. Mixtures of argon and nitrogen, argon and oxygen or argon and methane/acetylene are used for sputtering in reactive sputter deposition. In some cases, energetic ions of the target material can bombard the target producing "self-sputtering." This effect is important in ion plating using ionized condensable ions ("film ions") formed by arc vaporization or by post-vaporization ionization of sputtered or thermally evaporated atoms.

6.2.2 Sputtering Yields

The sputtering yield is the ratio of the number of atoms ejected to the number of incident bombarding particles and depends on the chemical

bonding of the target atoms and the energy transferred by collision. The sputtering yields of various materials bombarded by a variety of ion masses and energies have been determined experimentally[17]–[19] and have been calculated from first principles using Monte Carlo techniques.[20] Table 6-1 shows some masses of gaseous ions and target materials and the approximate sputtering yield by bombardment at the energies indicated.[21] Figure 6-3 shows some sputtering yields by argon ion bombardment as a function of ion energy. Note that the sputtering yields are generally less than one at bombarding energies of several hundred electron volts, indicating the large amount of energy input necessary to eject one atom. Sputtering is much less energy efficient than thermal vaporization and the vaporization rates are much lower than can be attained by thermal vaporization.

Table 6-1. Sputtering Yields by 500 eV Ions[21]

	Be (9)	Al (27)	Si(28)	Cu (64)	Ag (106)	W (184)	Au (197)
He^+ (4 amu)	0.24	0.16	0.13	0.24	0.2	0.01	0.07
Ne^+ (20 amu)	0.42	0.73	0.48	1.8	1.7	0.28	1.08
Ar^+ (40 amu)	0.51	1.05	0.50	2.35	2.4-3.1	0.57	2.4
Kr^+ (84 amu)	0.48	0.96	0.50	2.35	3.1	0.9	3.06
Xe^+ (131 amu)	0.35	0.82	0.42	2.05	3.3	1.0	3.01

For off-normal bombardment, the sputtering yield initially increases to a maximum then decreases rapidly as the bombarding particles are reflected from the surface[22] and this effect is called the "angle-of-incidence effect" as shown in Fig. 6-4. The maximum sputtering yield for argon generally occurs at about 70 degrees off-normal but this varies with the relative masses of the bombarding and target species. The increase of sputtering yield from normal incidence to the maximum can be as much as an increase of 2 to 3 times.

The preferential sputtering of different crystallographic planes in a polycrystalline sputtering target is used for sputter etching in metallographic sample preparation and can lead to roughening of the target surface with use.[23] The angle-of-incidence effect on sputtering yield and surface

mobility effects, can give rise to the development of surface features such as cones and whiskers on the target surface as shown in Fig 2-15. The roughening and feature-formation can lead to the decrease of the sputtering yield of the target surface as it goes from a smooth to a rough morphology. Roughening and preferential sputtering, along with stress from fabrication, can also lead to particulate generation from the target for some target materials.

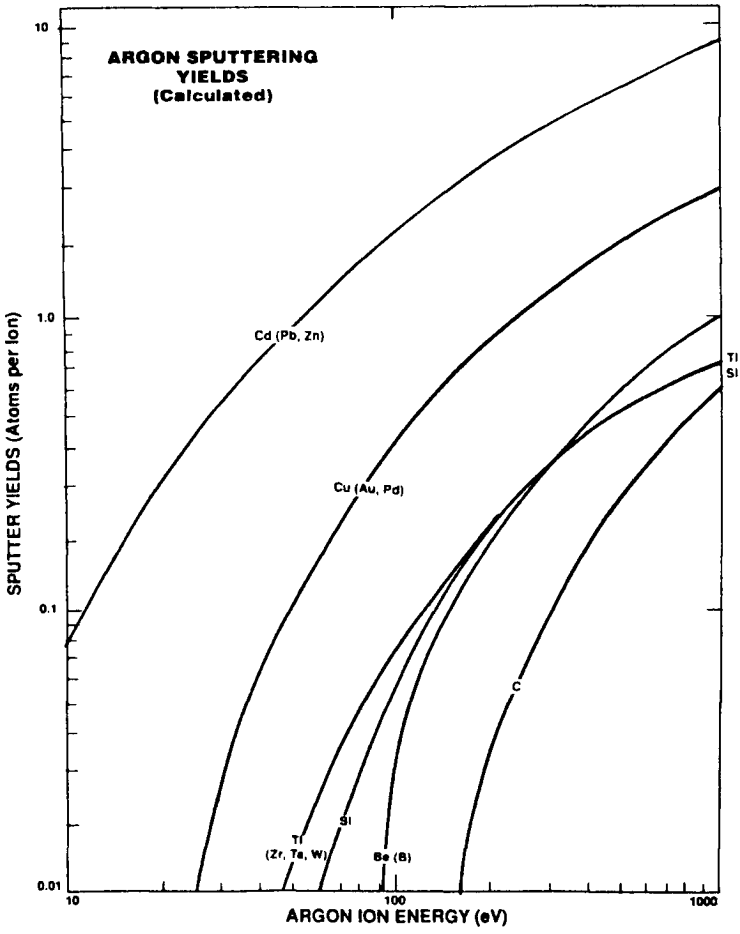


Figure 6-3. Some calculated sputtering yields (adapted from Ref. 20).

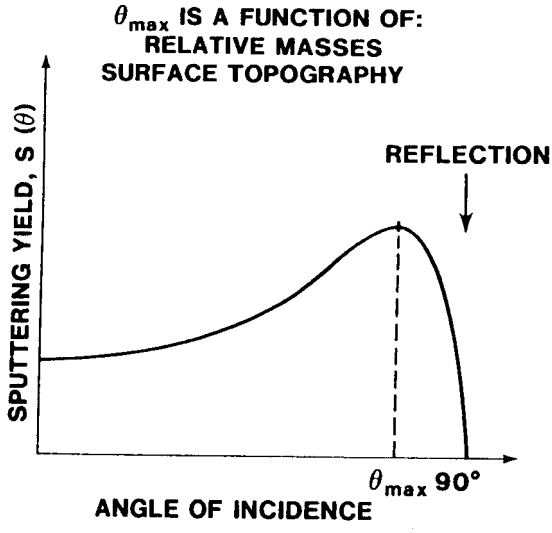


Figure 6-4. Sputtering yield as a function of angle-of-incidence of the bombarding ion.

The sputtering threshold energy is a rather vague number that is the lowest energy of the bombarding particle that can cause sputtering. Generally it is considered that incident particle energies of less than about 25 eV will not cause physical sputtering of an element. This is about the energy needed for atomic displacement in the radiation damage in solids.[24]

6.2.3 Sputtering of Alloys and Mixtures

Since sputtering is generally done from a solid surface ideally, if there is no diffusion, each layer of atoms must be removed from the surface before the next layer is subject to sputtering as shown in Fig. 6-5. This means that the flux of sputtered atoms has the same composition as the bulk composition of the sputtering target although, at any instant, the surface layer of the target will be enriched with the material having the lower sputtering yield.[25] In some cases where the mixture is of materials having significantly different masses or sputtering yields, the sputtered composition may be different than the target composition. For example, carbon on a copper surface will form islands which have a low sputtering yield,

and tungsten atoms on an aluminum surface will move around on the surface rather than sputter.

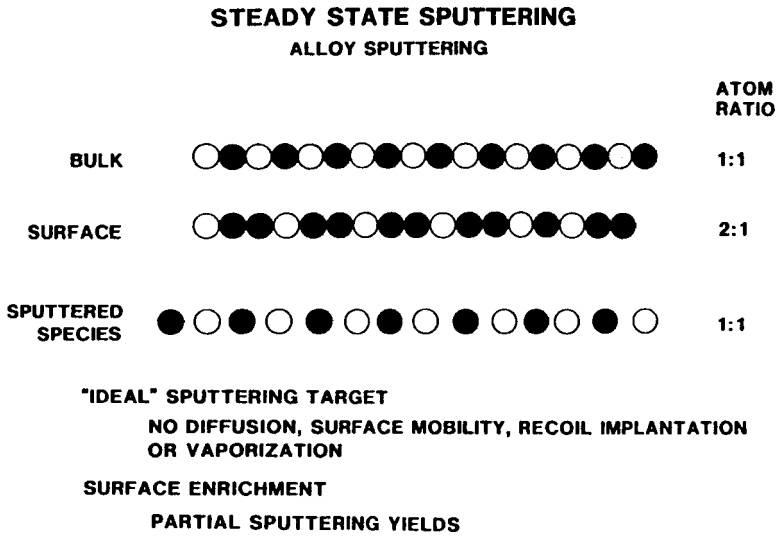


Figure 6-5. Sputtering, layer-by-layer.

6.2.4 Sputtering Compounds

Many compounds have chemical bonds that are stronger than those of the elements and thus have lower sputtering yields than the elements. For example, the sputtering yield of TiO_2 is about one tenth that of titanium. Compounds generally sputter by preferentially losing some of the more volatile constituent of the molecule (i.e., oxygen from TiO_2) so the sputtering surface is generally enriched in the less volatile constituent.[25][26] Often some of the lighter and more volatile species are lost in the transport between the target and the substrate or there is a less than unity reaction probability with the more condensable species on the surface of the depositing material (Sec. 9.5). This leads to a loss of stoichiometry in the deposited film compared to the target material. This loss is often made-up by some degree of reactive deposition.

In sputtering targets composed of several materials with greatly differing electronegativities, such as the oxides, there may be significant numbers of negative ions sputtered and accelerated away from the cathodic

target. These high energy ions can then bombard the growing material, causing sputtering and other bombardment effects. This has been found to be a particularly important effect when rf sputter depositing the high transition temperature (T_c) superconductor oxides, such as yittrum-barium-copper-oxides where the oxygen and barium have greatly differing electronegativites. The negative ions can completely resputter the depositing material. To avoid this effect ,the substrates can be mounted in an off-axis position[27][28] or a negative bias can be applied to the substrate.[29]

6.2.5 Distribution of Sputtered Flux

Atoms ejected from a flat, elemental, homogeneous, fine-grained (or amorphous) surface by sputtering, using near-normal high energy incidence particle bombardment, come off with a cosine distribution as shown in Fig. 5-4. Thus a sputtering surface can be treated as a series of overlapping point vaporization sources. Since sputtering is usually from large areas, the angular distribution of the depositing flux at a point on the substrate is large in contrast to vacuum evaporation where the angular distribution is typically small.

If the bombarding flux is off-normal to the target surface, the ejected flux will still have a cosine distribution if the incident particle energy is high, but is skewed in a forward direction if the incident particle energy is low. When an alloy target is sputtered, the off-cosine distribution with oblique angle bombardment will be different for the various masses with the most massive having the most off-cosine distribution.

The energy distribution of the ejected particles will depend on the bombarding species and bombarding angle. Oblique bombardment produces higher fractions of high energy ejected particles. Figure 6-6 shows the relative energies of thermally evaporated and sputtered copper atoms.

6.3 SPUTTERING CONFIGURATIONS

The most common form of sputtering is plasma-based sputtering where a plasma is present and positive ions are accelerated to the target which is at a negative potential with respect to the plasma. At low pressures, these ions reach the target surface with an energy given by the potential drop between the surface and the point in the electric field that the

ion is formed. At higher pressures, the ions suffer physical collisions and charge exchange collisions so there is a spectrum of energies of the ions and neutrals bombarding the target surface. Often the current in the cathode circuit is used to indicate the current density (ma/cm^2) or power (watts/cm^2) on the target. This measurement is only relative since it does not distinguish the bombardment by the positive ions from the emission of secondary electrons, and does not account for the flux of energetic neutrals from charge exchange processes.

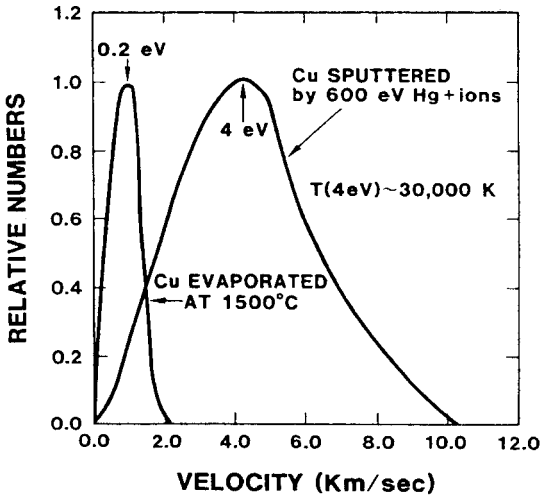


Figure 6-6. Energy distribution of sputtered and thermally evaporated copper atoms.

In vacuum-based sputtering an ion or plasma beam is formed in a separate ionization source, accelerated and extracted into a processing chamber which is under good vacuum conditions. In this process, the mean bombarding energy is generally higher than in the plasma-based bombardment and the reflected high energy neutrals are more energetic. Ion beam sputtering has the advantage that the flux and energy of the bombarding ions can be well regulated.

6.3.1 Cold Cathode DC Diode Sputtering

In a DC diode discharge (Sec. 4.4.3), the cathode electrode is the sputtering target and often the substrate is placed on the anode which is often at ground potential.[21][30] The applied potential appears across a region very near the cathode and the plasma generation region is very near the cathode surface. To establish a cold cathode DC diode discharge in argon, the gas pressure must be greater than about 10 mTorr and the plasma generation region is about one centimeter in width. At the cathode there is a spectrum of energies of the charged and neutral energetic species, due to change exchange and physical collisions as the particles cross the cathode dark space. The mean energy of the bombarding species is often less than $^1/_3$ of the applied potential.

In the cold cathode DC diode discharge, secondary electrons from the target surface are accelerated away from the cathode. These high energy electrons collide with atoms, creating ions. Some of the high energy electrons can bombard surfaces in the discharge chamber resulting in heating which may be undesirable. The cold-cathode DC discharge can be sustained at argon gas pressures higher than about 10 microns. At these pressures, atoms sputtered from a cathode surface are rapidly thermalized by collisions in the gas phase. Above about 100 mTorr, material sputtered from the surface is scattered back to the electrode and sputter deposition is not possible.

The cathode in DC diode discharge must be an electrical conductor since an insulating surface will develop a surface charge that will prevent ion bombardment of the surface. If the target is initially a good electrical conductor but develops a non-conducting or poorly-conducting surface layer, due to reaction with gases in the plasma, surface charge buildup will cause arcing on the surface. This “poisoning” of the target surface can be due to contaminant gases in the system or can develop during reactive sputter deposition from the deliberately introduced process gases.[31]

The DC diode configuration is used to sputter deposit simple, electrically conductive materials, although the process is rather slow and expensive compared to vacuum deposition. An advantage to a DC diode sputtering configuration is that a plasma can be established uniformly over a large area so that a solid large-area vaporization source can be established. This surface need not be planar but can be shaped so as to be conformal to a substrate surface. For example, the sputtering target can be a section of a cone that is conformal to a conical surface that is rotated in front of the target.

A problem can exist at the edges of the sputtering target where a ground shield, used to confine the plasma generation region, causes curvature of the electrical equipotential surfaces. The ions are accelerated normal to the equipotential surfaces and this curvature causes focusing of the ion bombardment and uneven sputter-erosion of the surface as shown in Fig. 4-2. The problem can be minimized by having a target area that is greater that the substrate size, using moving fixturing and/or by using deposition masks.

6.3.2 DC Triode Sputtering

In triode DC sputtering, a separate plasma is established in front of the sputtering target usually using a hot filament or hollow cathode as the source of electrons, and magnetic confinement along the cathode-anode axis. Ions for sputtering are then extracted from the plasma by applying a negative potential to the target. Sputter deposition is on substrates facing the sputtering target. Such a plasma can be established at a much lower pressure than the cold cathode DC diode configuration. A disadvantage of this configuration is the non-uniform plasma density over the surface of the target. This leads to uneven erosion and deposition. Since the advent of magnetron sputtering, this technique is not used very much but is capable of achieving high sputtering rates.[32][33]

6.3.3 AC Sputtering

In alternating current (AC) sputtering, the potential on the target is periodically reversed. At frequencies below about 50 kHz the ions have enough mobility so that a DC diode-like discharge, where the total potential drop is near the cathode, can be formed alternately on each electrode. The substrate, chamber walls or another sputtering target can be used as the counterelectrode. In asymmetrical AC sputtering the substrate is made the counterelectrode and the depositing film is periodically "backsputtered" to enhanced film purity.[34] A problem with reactive sputter deposition of electrically insulating films is that the deposition of the insulating film on the chamber walls can cause the anode area and position to change and this has been called the "disappearing anode" problem. AC magnetron sputtering at 50–100 kHz can be used in dual target configuration to eliminate the disappearing anode problem by making a target surface a clean anode during each half cycle.

6.3.4 Radio Frequency (rf) Sputtering

At frequencies above 50 kHz, the ions do not have enough mobility to allow establishing a DC diode-like discharge and the applied potential is felt throughout the space between the electrodes. The electrons acquire sufficient energy to cause ionizing collisions in the space between the electrodes and thus the plasma generation takes place throughout the space between the electrodes. When an rf potential, with a large peak-to-peak voltage, is capacitively coupled to an electrode, an alternating positive/negative potential appears on the surface. During part of each half-cycle, the potential is such that ions are accelerated to the surface with enough energy to cause sputtering while on alternate half-cycles, electrons reach the surface to prevent any charge buildup. Rf frequencies used for sputter deposition are in the range of 0.5–30 MHz with 13.56 MHz being a commercial frequency that is often used. Rf sputtering can be performed at low gas pressures (<1 mTorr).

Since the target is capacitively coupled to the plasma it makes no difference whether the target surface is electrically conductive or insulating although there will be some dielectric loss if the target is an insulator. If an insulating target material, backed by a metal electrode is used, the insulator should cover the whole of the metal surface since exposed metal will tend to short-out the capacitance formed by the metal-insulator-sheath-plasma.

Rf sputtering can be used to sputter electrically insulating materials although the sputtering rate is low. A major disadvantage in rf sputtering of dielectric targets, is that most electrically insulating materials have poor thermal conductivity, high coefficients of thermal expansion, and are usually brittle materials. Since most of the bombarding energy produces heat, this means that large thermal gradients can be generated that result in fracturing the target if high power levels are used. High rate rf sputtering is generally limited to the sputter deposition from targets of silicon dioxide (SiO_2) which has a low coefficient of thermal expansion and thus is not very susceptible to thermal shock. In some cases, 48 hours is used to rf sputter-deposit a film of SiO_2 several microns thick.

6.3.5 DC Magnetron Sputtering

In DC diode sputtering, the electrons that are ejected from the cathode are accelerated away from the cathode and are not efficiently used for sustaining the discharge. By the suitable application of a magnetic

field, the electrons can be deflected to stay near the target surface and by an appropriate arrangement of the magnets, the electrons can be made to circulate on a closed path on the target surface. This high flux of electrons creates a high density plasma from which ions can be extracted to sputter the target material producing a magnetron sputtering configuration.[35]

The most common magnetron source is the planar magnetron where the sputter-erosion path is a closed circle or elongated circle ("race-track") on a flat surface.[35]–[37] A closed circulating path can easily be generated on any surface of revolution such as a post or spool,[16][38][39] inside of a hollow cylinder,[39] a conical section,[40]–[42] or a hemispherical section.[43] In the case of the post-cathode and hollow-cylinder cathode, a flange at the ends at a negative potential can be used to electrostatically contain electrons that would be lost from the cathode. Figure 6-7 shows some magnetron configurations.

The planar magnetron configuration forms a vaporization source that consists of two parallel lines that can be of almost any length. The post cathode source allows deposition on the inside of a cylinder or cylindrical fixture. This arrangement was first used over 25 years ago for depositing films on the edges of razor blades that were stacked around the post cathode.[44] Many razor blades are still coated the same way. The hollow cylindrical cathode is useful for coating three-dimensional parts since the flux comes from all directions. A substrate, such as a fiber, can be passed up the axis of the cylinder and continuously coated. The hollow cylinder has the added advantage that the material that is not deposited on the part, is deposited on the target and re-sputtered, giving good target material utilization. The conical target produces a very dispersed flux and is useful for coating large areas. The S-gun configuration can prevent the "disappearing anode effect" problem by continuously depositing pure metal on a shielded anode. The hemispherical target is an example of a conformal target that is used in coating a hemispherical substrate.

The principal advantage to the magnetron sputtering configuration is that a dense plasma can be formed near the cathode at low pressures so that ions can be accelerated from the plasma to the cathode without loss of energy due to physical and charge-exchange collisions. This allows a high sputtering rate with a lower potential on the target than with the DC diode configuration. This configuration allows the sputtering at low pressures (<5 mTorr), where there is no thermalization of particles from the cathode, as well as at higher pressures (>5 mTorr) where thermalization occurs.

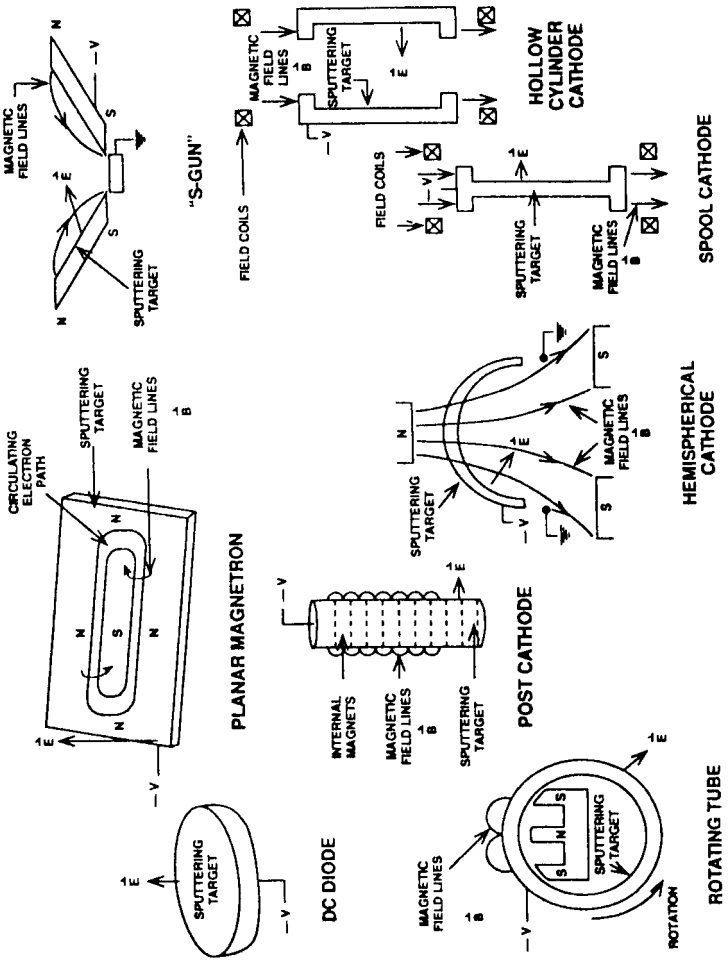


Figure 6-7. Planar, post, hollow cylinder, conical and hemispherical magnetrons.

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One disadvantage of the planar magnetron configuration is that the plasma is not uniform over the target surface. Therefore the deposition pattern is dependent on the position of the substrate with respect to the target. This means that various types of fixturing must be used to establish position equivalency for the substrate(s). The non-uniform plasma also means that target utilization is non-uniform, sometimes with only 10–30% of the target material being used before the target is scrapped. A great deal of effort has been put forth to improve utilization of the target material.

One commercial target design for improving material utilization utilizes magnetic polepieces that extend above the target surface. This design allows the magnetic field to be more parallel to the target surface. As the target erodes, it must be moved forward to keep the target surface in the same position. In another commercial design, the racetrack configuration is formed on the surface of a rotating tube to give the "rotatable cylindrical (tubular) magnetron."[45] In other designs, the magnetic field is moved behind the target.

The density of the plasma in the vicinity of the cathode can be augmented by injecting electrons from a hot filament or a hollow cathode.[46][47] This increases the sputtering rate that can be attained from a magnetron source. It also can allow the sputtering discharge to be operated at a lower pressure.

The magnetic field in magnetron sputtering can be formed using permanent magnets or electromagnetics or a combination of the two. The magnetics can be internal to the target, such as in the planar magnetron, or can be external to the target. In the case of the post cathode, the magnetic field can be formed using a Helmholtz-coil arrangement and the magnetic field can be "tuned" over the surface of the post by adjusting the current flow through the field coils.[36]

Unbalanced Magnetron

Another disadvantage of the magnetron sputtering configurations is that the plasma is confined near the cathode and is not available to activate reactive gases in a plasma near the substrate for reactive sputter deposition or for ion plating. This disadvantage can be overcome by applying an rf bias to the cathode along with the DC potential, to generate a plasma away from the cathode or by having an auxiliary plasma near the substrate surface. Alternatively, an unbalanced magnetron configuration can be used where the magnetic field is such that some electrons can escape

from the cathode region (Sec. 4.4.4).[48]–[55] A disadvantage of the unbalanced magnetron is that the flux of escaping electrons is not uniform and thus the plasma generated in not uniform.

Because the magnetron configuration does not uniformly erode the total cathode surface, some of the surface area can be poisoned and accumulate compound film material when performing reactive deposition. These areas can allow a surface charge to buildup causing arcing over the target surface. This problem can be overcome by applying an rf potential to the target along with the DC potential. When applying an rf potential along with the DC potential an rf choke should be placed in the DC circuit to prevent rf power from entering the DC power supply.

6.3.6 Pulsed DC Magnetron Sputtering

The pulsed DC magnetron sputtering technique uses a unipolar or bipolar square waveform operating at 50–250kHz.[56]–[62] The symmetrical pulsed DC can be used in a dual magnetron sputtering configuration where each of the magnetrons are alternately biased positively and negatively. This helps to eliminate the "disappearing anode" effect found when sputter depositing electrically insulating films with continuous DC power. This technique can be used to reactively sputter non-conductive oxide targets.

In sputter deposition using pulsed DC, the optimal frequency of pulsing, the pulse duration, and the relative pulse heights, depend on the material being sputtered and deposited. For example, when reactively sputtering a good dielectric material such as Al_2O_3, a frequency of about 50kHz is best, but when sputter depositing a somewhat conductive film material such as TiN or ITO, a higher frequency (150 kHz) is best due to the conduction of the surface charge away from the surface.[63]

6.3.7 Ion and Plasma Beam Sputtering

In an ion beam sputtering system, ions are generated in a separate chamber, extracted into the sputtering chamber and sputter a target in a relatively good vacuum environment.[64][65] In some ion sources such as the Kaufman ion source, the energy of the ions is rather well defined. In other ion sources, the ion energies are not well defined. In many ion beam sources the ion flux can vary across the beam diameter, particularly if the ion beam has not been "neutralized."

After a pure ion beam has been extracted from an ion source, electrons may be added to the ion beam to form a plasma beam which will not diverge and not cause a charge build-up on the target surface. In the Kaufman source these electrons are from a hot filament ("neutralizer filament"). It should be noted that the ions are not neutralized. Instead the beam is volumetrically neutral due to the addition of the electrons.

Plasma beams can be generated without separation of the ions from the electrons. Plasma beams have the advantage that the electrons can easily be deflected (steered) by a magnetic or electrostatic field and the ions will follow. It should be noted that a pure ion beam is more difficult to steer.

Ion and plasma beam sputtering have the advantage that they can be performed in a good vacuum and at a high pumping speed. Therefore contamination can easily be controlled. Also the flux and energy of the bombarding particles can easily be monitored and controlled, and insulating surfaces can be sputtered. Disadvantages can include: (a) the high flux of reflected neutrals that can bombard the substrate since there is no thermalization in the deposition system, (b) the small beam area and (c) the relatively high cost. Ion beam sputter deposition is used in depositing some high-performance optical coatings. Ion beams are used for sputter cleaning, sputter etching, and in the IBAD process (Sec. 8.7).

6.4 TRANSPORT OF THE SPUTTER-VAPORIZED SPECIES

When atoms are vaporized from the sputtering target, they traverse the space between the target and the substrate. In sputter deposition this distance can be made short compared to that normally used in thermal evaporation since there is little radiant heating from the target.

6.4.1 Thermalization

Thermalization is the reduction of the energy of high energy particles to the energy of the ambient gas by collisions as the particle moves through the gas (Sec. 3.2.2). The pressure and distance for thermalization depend on the relative masses of the particles and the collision probability as shown in Fig. 3-3. Generally in high-pressure sputtering (>5 mTorr pressure) the ejected particles are thermalized before they reach the

substrate and in low-pressure sputtering (<5 mTorr) many of the energetic sputtered atoms reach the substrate with their ejection energies. Reflected high energy neutrals can reach the substrate without thermalization.

6.4.2 Scattering

Sputtered atoms leave each point on the target surface with a cosine distribution. At sputtering pressures above a few mTorr, gas scattering can modify the flux distribution from the sputtering target. At higher pressures (>10 mTorr) a portion of the sputtered material is scattered back to the target.[66] At the higher pressures, material sputtered from one target may be scattered so as to contaminate areas out of line-of-sight of the target or may contaminate the other target surfaces if the system is a multiple-target system. This effect is called target "cross-talk." In case such a problem exists, shutters and dividers should be used to isolate the deposition regions to prevent "cross-talk." In some cases, scattering may be used to advantage to improve the surface coverage by randomizing the flux direction.

6.4.3 Collimation

Sputtering from a large area source produces a vapor flux that has a wide distribution of angle-of-incidence at the substrate surface. To produce a more normal incidence pattern, the sputtered atoms can be collimated using a honeycomb-shaped baffle between the target and the substrate.[67]–[70] This collimation tends to decrease the tendency of the deposition to produce a columnar morphology in the deposited film and enhances the filling of vias in semiconductor device fabrication. Collimation can also be attained by postvaporization ionization of the vaporized material and accelerating the ions to the substrate surface.

6.4.4 Postvaporization Ionization

In sputtering, the sputtered particles are neutral when they leave the target surface (except in the case of negative ions) and few particles are ionized in the plasma, particularly in the magnetron configuration, where there is a short path length through the plasma. Ionization can be enhanced by having an flux of energetic (100 eV) electrons between the target and the substrate to produce postvaporization ionization. Ionization values as high as 70% have

been reported using an rf-excited plasma.[71][72] These film ions can be accelerated to the substrate surface by applying a potential to the surface. This tends to give a more-normal direction to the depositing flux and aids in filling vias in semiconductor processing. It is reported that 0.25 micron diameter vias with an aspect ratio of 6:1 can be filled using this technique.[73] There has been some work on sustaining the sputtering plasma using only ions of the target material and to sputter the target with the film ions (self-sputtering).[74]–[76]

6.5 CONDENSATION OF SPUTTERED SPECIES

In sputter deposition, the sputtered particles condense on the substrate surface and give up energy. Substrate heating arises not only from the condensation energy of the depositing adatoms, but also from the high kinetic energy of the depositing particles, particularly at low pressures where the particles have not been thermalized. Substrate heating can also arise from plasma effects such as radiation and surface recombination. Energetic neutral bombardment can also contribute to substrate heating during deposition. Heating can range from 15–100 eV per deposited atom for materials sputter deposited in a magnetron system[77] compared to a few eV from condensation alone.

In plasma-based sputter deposition, a negative bias may be deliberately applied to the substrate during deposition in order to have concurrent energetic particle bombardment. In addition, the substrate may assume a self-bias with respect to the plasma and this may give continuous bombardment during deposition. This bias sputter deposition was first described by Maissel and Schaible in 1965 who noted that the concurrent bombardment during deposition reduced the contamination in sputter deposited chromium films. "Bias sputtering" is often described in the literature as a means for improving the surface coverage and planarization of patterned semiconductor devices.[78]–[85] This technique can be considered as a type of ion plating (Ch. 8).

6.5.1 Elemental and Alloy Deposition

Sputter deposition is used to deposit films of elemental materials. However, one of its advantages is that it can deposit alloy films and maintain the composition of the target material by virtue of the fact that the

material is removed from the target layer-by-layer. This allows the deposition of some rather complex alloys such as W:Ti for semiconductor metallization,[86] Al:Si:Cu for semiconductor metallization,[87] and M(etal)-Cr-Al-Y alloys for aircraft turbine blade coatings.

6.5.2 Reactive Sputter Deposition

Reactive sputter deposition from an elemental target[88][89] relies on: (a) the reaction of the depositing species with a gaseous species, such as oxygen or nitrogen, (b) reaction with an adsorbed species, or (c) reaction with a co-depositing species such as carbon to form a compound. The reactive gas may be in the molecular state (e.g., N_2, O_2) or may be "activated" to form a more chemically reactive or more easily adsorbed species. Typically, the reactive gases have a low atomic masses (N=14, O=16) and are thus not effective in sputtering. It is therefore desirable to have a heavier inert gas, such as argon, to aid in sputtering. Mixing argon with the reactive gas also aids in activating the reactive gas by the Penning ionization/excitation processes.

Typically, a problem in reactive sputter deposition is to prevent the "poisoning" of the sputtering target by the formation of a compound layer on its surface.[31] Poisoning of a target surface greatly reduces the sputtering rate and sputtering efficiency. This problem is controlled by having a high sputtering rate (magnetron sputtering) and controlling the availability of the reactive gas, such that there will be enough reactive species to react with the film surface to deposit the desired compound, but not so much that it will unduly poison the target surface.

The appropriate gas composition and flow for reactive sputter deposition can be established by monitoring the partial pressure of the reactive gas as a function of reactive gas flow,[90]–[93] or by impedance of the plasma discharge. Figure 6-8 shows the effect of reactive gas flow on the partial pressure of the reactive gas in the reactive sputter deposition of TiN. Under operating conditions of maximum flow and near-minimum partial pressure, the deposit is gold-colored TiN and the sputtering rate is the same as metallic titanium. At higher partial pressures, the sputtering rate decreases and the film is brownish. As the target is poisoned, the deposition rate decreases. When the nitrogen availability is decreased, the target is sputter-cleaned and the deposition rate rises.

The gas composition should be determined for each deposition system and fixture geometry. A typical mixture for reactive sputter

deposition might be 20% nitrogen and 80% argon where the partial pressure of nitrogen during deposition is 2 x 10^{-4} Torr and the total gas flow is 125 sccm. Gases mixtures are typically controlled using individual mass flow meters on separate gas sources though specific gas mixtures can be purchased. Figure 6-9 depicts a typical reactive sputter deposition system.

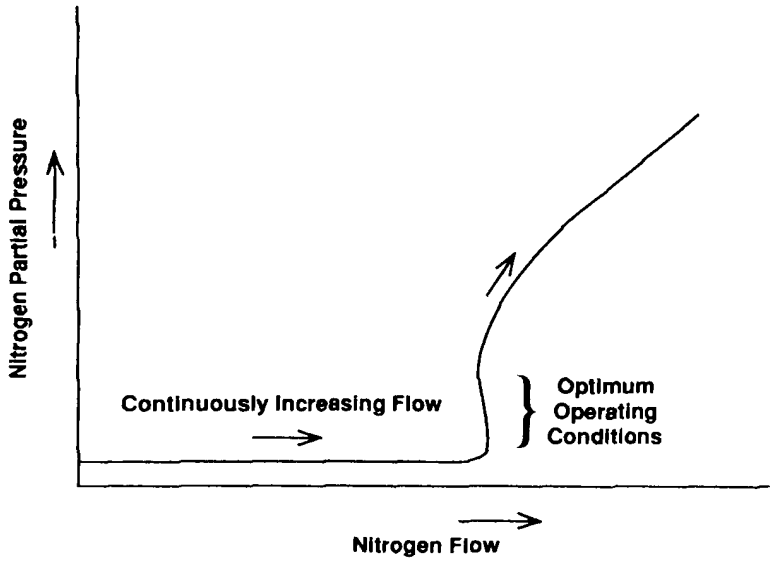


Figure 6-8. Nitrogen partial pressure and flow conditions for the reactive sputter deposition of TiN with constant target power (adapted from Ref. 51).

In reactive deposition, the reactive gases are being pumped ("getter pumping") by the depositing film material. Since the depositing film is reacting with the reactive gas, changes in the area or rate of the film being deposited will change the reactive gas availability and the film properties. Thus, it is important to use the same fixture, substrate, and vacuum surface areas as well as deposition rate, in order to have a reproducible reactive sputter deposition process. Changes in the geometry (loading factor) or deposition rate will necessitate changes in gas flow parameters.[90] The gas density (partial pressure) of the reactive gas in the plasma can be monitored by optical emission spectroscopy or mass spectrometry techniques.[91]–[93]

Since gas pressure is important to the properties of the sputter deposited film it is important that the vacuum gauge be periodically calibrated and located properly and pressure variations in the chamber be minimized.

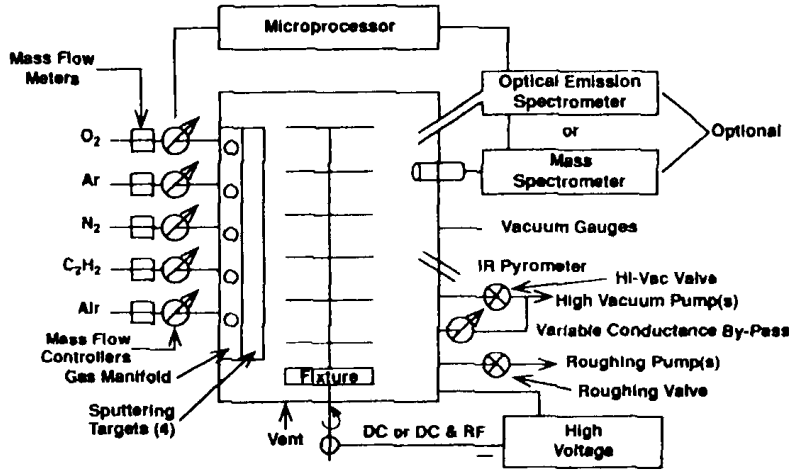


Figure 6-9. Typical reactive sputter deposition system.

In some reactive deposition configurations, the inert gas is injected around the sputtering target and the reactive gas is injected near the substrate surface. This inert "gas blanket" over the target surface is helpful in reducing target poisoning in some cases.

In reactive deposition, the depositing material must react rapidly or it will be buried by subsequent depositing material. Therefore, the reaction rate is an important consideration. The reaction rate is determined by the reactivity of the reactive species, their availability, and the temperature of the surface. The reactive species can be activated by a number of processes including:

- Dissociation of molecular species to more chemically reactive radicals (e.g., $N_2 + e^- \rightarrow 2N^o$ and $NH_3 + e^- \rightarrow N^o + 3H^o$)
- Production of new molecular species that are more chemically reactive and/or more easily absorbed on surfaces (e.g., $O_2 + e^- \rightarrow 2O^o$ then $O^o + O_2 \rightarrow O_3$)
- Production of ions—recombination at surfaces releases energy

- Adding internal energy to atoms and molecules by creating metastable excited states—de-excitation at surfaces releases energy
- Increasing the temperature of the gas
- Generating short wavelength photons (UV) that can stimulate chemical reactions
- Generating energetic electrons that stimulate chemical reactions
- Ions accelerated from the plasma to the surface promotes chemical reactions on the surface (bombardment enhanced chemical reactions)

The extent to which a plasma can activate the reactive gases and provide ions for concurrent bombardment depends on the properties of the plasma and its location. In many sputtering systems the plasma conditions vary widely throughout the deposition chamber. This is particularly true for the magnetron configurations where the sputtering plasma is confined near the target. In such a case, a plasma needs to be established near the substrate surface to activate reactive gases and provide ions for concurrent bombardment. This can be done using an unbalanced magnetron configuration, application of an rf to the target, or by establishing a separate auxiliary plasma over the substrate surface.

The reaction probability is also a function of the surface coverage. For example, it is easier for an oxygen species to react with a pure titanium surface than with a $TiO_{1.9}$ surface. Figure 6-10 shows the effect of reactive nitrogen availability on the electrical resistivity of TiN_x films. The films have minimum resistivity when the composition is pure titanium and when the composition is near TiN.

Another important variable in reactive deposition is concurrent bombardment of the depositing/reacting species by energetic ions accelerated from the plasma ("sputter ion plating" or "bias sputtering"). Concurrent bombardment enhances chemical reactions and can densify the depositing film if unreacted gas is not incorporated into the deposit. Bombardment is obtained by having the surface at a negative potential (applied bias or self-bias) so that ions are accelerated from the plasma to the surface. Figure 6-11 shows the relative effects of deposition temperature and applied bias on the electrical resistivity (normalized) of a TiN_x film.[94] The lowest resistivity is attained with both a high deposition temperature and concurrent bombardment although a low-temperature deposition with concurrent bombardment comes close.

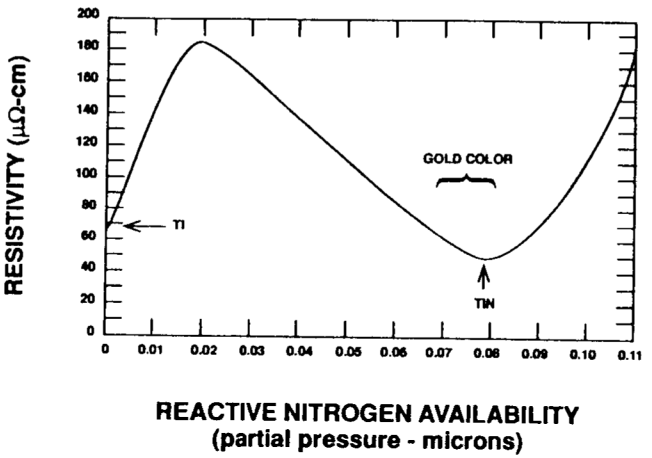


Figure 6-10. TiN resistivity as a function of nitrogen content (nitrogen availability during deposition). (Adapted from Ref. 94.)

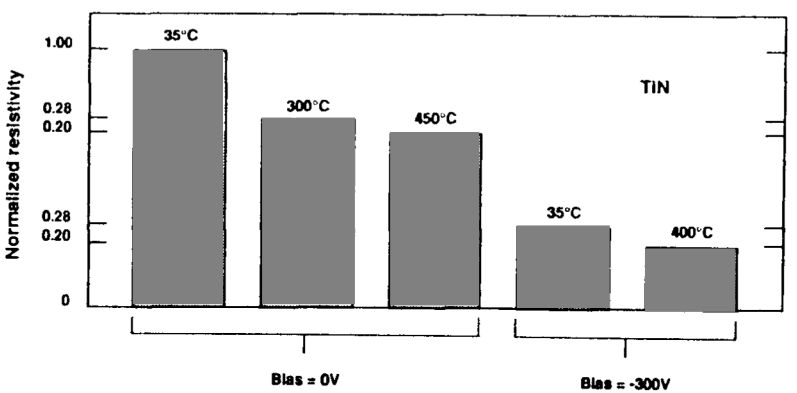


Figure 6-11. TiN resistivity as a function of deposition temperature and concurrent bombardment (adapted from Ref. 94).

Reactive deposition is used to produce colored wear-resistant decorative coatings such as TiN (gold), TiC_xN_y (bronze, rose, violet, or black as x and y are varied) and ZrN (brass). Coatings such as TiN and $(Ti,Al)C_xN_y$ are used as wear-resistant coatings on tools, molds, and other surfaces. Reactive deposition is used to produce oxide films such as ZrO_2 and TiO_2, which are used to form anti-reflection and band-pass coatings on

optical components, indium-tin-oxide (ITO), is a transparent electrical conductor and $SiO_{1.8}$, is a material of interest as a transparent, moisture-permeation-barrier materials for packaging applications.

The co-depositing material for reactive deposition can be from a second sputtering target. However it is often in the form of a chemical vapor precursor which is decomposed in a plasma and on the surface. Chemical vapor precursors are such materials as acetylene (C_2H_2) or methane (CH_4) for carbon, silane (SiH_4) for silicon, and diborane (B_2H_6) for boron. This technique is thus a combination of sputter deposition and plasma enhanced chemical vapor deposition and is used to deposit materials such as the carbides, borides, and silicides.[95] It should be noted that co-deposition does not necessarily mean reaction. For example, carbon can be deposited with titanium to give a mixture of Ti + C but the deposit may have little TiC.

In reactive sputtering, the injection of the reactive gas is important to insure uniform activation and availability over the substrate surface. This can be difficult if, for instance, the film is being deposited over a large area such as on 10' x 12' architectural glass panels where the sputtering cathode can be twelve feet or more in length. In such an application, it may be easier to use quasi-reactive sputtering from a compound target.

In "quasi-reactive sputter deposition" the sputtering target is made from the compound material to be deposited and a partial pressure of reactive gas in a plasma is used to make-up for the loss of the portion of the gaseous constituent that is lost in the transport and condensation/reaction processes. Typically the partial pressure of the reactive gas used in quasi-reactive deposition is much less than that used for reactive deposition. For example, the gas composition might be 10% oxygen and 90% argon.

6.5.3 Deposition of Layered and Graded Composition Structures

Layered structures can be deposited by passing the substrate in front of several sputtering targets sequentially. For example, X-ray diffraction films are formed by depositing thousands of alternating layers of high-Z (W) and low-Z (C) material with each layer being about 30Å thick.

Layered and graded composition structures can be deposited using reactive deposition. The composition is changed by changing the availability of the reactive gas. Thus one can form layers of Ti-TiN-Ti by changing the availability of the nitrogen. Since nitrogen has been incorporated in the

titanium target surface during sputtering in a nitrogen-containing plasma, it takes some time for pure titanium to be deposited from the target when the plasma is changed to just contain argon.

A single target may be used to deposit layered structures. For example, by precoating the target with the material to be deposited first, a layered structure is formed by the sputtering first removing the surface material and then the bulk material by sputtering. This will also give a "graded interface" since the surface coating will not be removed completely before the bulk material is exposed. An example of this approach is the use of chromium on a molybdenum target so that the chromium is deposited first. The chromium underlayer improves the adhesion of the molybdenum film to many surfaces. The chromium can be deposited on the molybdenum sputtering target by sublimation prior to each deposition run.

6.5.4 Deposition of Composite Films

Composite films are those containing two or more phases. Composite films often will be deposited in reactive deposition processes if there is not enough reactive gas available or if there is a mixture of reactive gases. The properties of composite films depend not only on the composition but the size and distribution of the separate phases. Metals can be co-deposited with polymers to form a polymer-metal composite film. This can be done by combining physical sputtering with plasma polymerization.[96]

6.5.5 Some Properties of Sputter Deposited Thin Films

In non-reactive sputter deposition, the properties of the film depends to a large extent on the gas pressure which determines the thermalization of the reflected high energy neutrals and the sputtered species. The energy of the species striking the surface of the growing film affects the development of the columnar morphology, density, and the residual film stress.[16][97][98] In reactive sputter deposition, the availability of the activated reactive species is important in determining the stoichiometry of the deposited film. For reproducible film properties it is important that the gas pressure and composition be reproducible and the geometry of the system be constant.

6.6 SPUTTER DEPOSITION GEOMETRIES

The geometry of the sputter deposition system determines many of the factors that affect the properties of the deposited film and the throughput of the system. There are numerous combinations of possible geometries. A specific geometry has to be determined for each application—what is good for coating one side of a flat plate will not be applicable to complete coverage of a 3-dimensional object. In some cases, pre-deposition processing and handling may be the controlling factor in throughput. For example, in a high-volume in-line sputter deposition system, cleaning and loading the substrates may be the limiting factor to the throughput.

6.6.1 Deposition Chamber Configurations

In Sec. 3.5.2 various deposition chamber geometries were discussed and depicted in Fig. 3-9. Sputtering has the advantage that the sputtering source provides a long-lived vaporization source that has a stable geometry. This allows sputtering to be easily adapted to lock-load and in-line systems. Sputter deposition also allows the close spacing between the target and the substrate which minimizes chamber volume but limits accessibility to the space between the target and the substrate for monitoring purposes.

6.6.2 Fixturing

Fixturing is discussed in Sec. 3.5.5 and some fixturing is shown in Fig. 3-12. In many cases, the substrates are moved in front of the sputtering target(s). In coating three-dimensional parts, the substrates should be rotated in front of the target(s) to insure that all areas of the part have the same distribution of the angle-of-incidence of the depositing flux. In situations where the substrate is passed over the target, the initial deposition is at a high angle-of-incidence. This exacerbates the development of a columnar morphology and shields may have to be used to prevent this initial high angle of incidence.

Substrates are often mounted on fixtures that are then mounted on tooling in the deposition chamber. Mounting may be by mechanical clamping, electrostatic attraction, or bonding by a removable adhesive. Substrates may be grounded or electrically biased through the fixture. The electrical condition should be the same for all substrates. The substrates may be heated or cooled by contact with the substrate holder as is necessary

for the processing. Temperature uniformity across the substrate holder and the substrate(s) is often required for the formation of reproducible material.

Deposited film uniformity can be improved by rotation and angular variation—this may be particularly necessary for non-planar surfaces such as stepped surfaces. By moving the substrates sequentially in front of sputtering sources, multilayer films can be produced. For example, thickness accuracy to better than 0.1 Å and a reproducibility of better than 0.1% have been reported for multilayer film structures used for x-ray/UV Bragg reflectors.

Concurrent ion bombardment during deposition can have a significant affect on film properties and this bombardment can be accomplished in some configurations by having an electrical bias on the film during deposition. The self-bias or applied bias on all substrates should be the same in order to have reproducible concurrent bombardment conditions. In order to attain this condition, the electrical contact between each of the substrates and the fixture should be good and reproducible. The fixture should be electrically floating, electrically biased, or should have a good ground connection to the deposition chamber.

Sputter deposition is often used to deposit magnetic thin films for recording. Sometimes it is desirable to have a magnetic bias on the substrate surface during deposition to influence the film growth. The use of a magnetic field in the vicinity of the target can affect sputtering target performance. The magnetic field may also extract electrons from the target to give unwanted electron bombardment of the growing film. This can be avoided by having a screen grid at a negative potential between the target and the substrate.

6.6.3 Target Configurations

Often more than one sputtering target is used in the deposition process. The targets and target clusters may be arranged sequentially[99] or with random access so that a multilayer film can be deposited. Some target arrangements are shown in Fig. 6-12.

When using dual, opposing (facing) unbalanced magnetron sources, the magnetic poles are oriented with the north pole of one magnetron opposite the south pole of the other magnetron and a confining plate, at a negative potential, is used above and below the sources to help contain the electrons and keep them from escaping from the inter-target region. Four or more targets can be arranged as shown in Fig. 6-12.[100] This arrangement approximates a cylindrical target and allows a more uniform distribution of incident flux on an object placed at the center.

Figure 6-12. Planar magnetron supttering target arrangements.

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6.6.4 Ion and Plasma Sources

In some types of reactive sputter deposition, a few monolayers of a pure metal are deposited and then the substrate is passed in front of a source of the reactive species. By doing this repeatedly, a compound film can be built-up. The source for reactive gas is generally a plasma source, such as a gridless end-Hall source, where the gas is activated and, in some cases, reactive ions are accelerated to the substrate (Sec. 4.5.1). An easy configuration for doing this is to mount the substrates on a drum and repeatedly rotate them in front of the sputtering source and the reactive gas source such as with the MetaMode™ deposition configuration.[101]

6.6.5 Plasma Activation Using Auxiliary Plasmas

Activation of the reactive species enhances chemical reactions during reactive deposition. The plasma used in sputtering will activate the reactive gases but often the plasma volume is small or not near the substrate surface. Configurations such as the unbalanced magnetron can expand the volume. Auxiliary electron sources can be used to enhance the plasma density between the target and the substrate.[102] Magnetic fields in the vicinity of the substrate can also be used to enhance reactive gas ionization and bombardment. For example using a magnetic field (100G) in the vicinity of the substrate, the ion flux was increased from 0.1 ma/cm^2 to 2.5 ma/cm^2 in the unbalanced magnetron reactive sputter deposition of Al_2O_3.[103]

6.7 TARGETS AND TARGET MATERIALS

For demanding applications, a number of sputtering target properties must be controlled in order to have reproducible processing.[104] The cost of large-area or shaped sputtering targets can be high. Sometimes by using a little ingenuity, cheaper configurations can be devised such as making large plates from overlapping mosaic tile, rods from stacked cylinders, etc. Conformal targets, which conform to the shape of the substrate, may be used to obtain uniform coverage over complex shapes and in some instances may be worth the increased cost.

6.7.1 Target Configurations

Targets can have many forms. They may have to be of some predetermined shape to fit supplied fixtures or be conformal to the substrate shape. For example conformal targets may be a sector of a cone for coating a rotating cone, hemispherical to coat a hemisphere, axial rod to coat the inside of a tube, etc. The targets may be moveable or be protected by shutters to allow "pre-sputtering" and "conditioning" of the target before sputter deposition begins. Common sputtering target configurations are the planar target, the hollow cylindrical target, the post cathode, the conical target, and the rotating cylindrical target.[105][106]

A single target may be used to deposit alloys and mixtures by having different areas of the target be of different materials. For example, the mosaic target may have tiles of several materials, the rod target may have cylinders of several materials, etc. The composition of the film can then be changed by changing the area ratios. When using this type of target, the pressure should be low so that backscattering does not give "cross-talk" between the target areas. If cross-talk occurs, the sputtering rates may change as one material is covered by the other which has a lower sputtering rate.

Multiple targets allow independent sputtering of materials and can be used to allow deposition of layers, alloys, graded compositions, etc. If both the targets and the substrates are stationary, the flux distribution from each target must be considered. Often when using large area targets, the substrates are rotated sequentially in front of the targets to give layered structures and mixed compositions

Targets of different materials can have different plasma characteristics in front of each cathode.[107] This can be due to differing secondary electron emission from the target surfaces. If the substrates are being rotated in front of the sputtering target(s), changes in the plasma may be observed depending of the position of the fixture, particularly if the fixture has a potential on it.

"Serial co-sputtering" is a term used for a deposition process where material from one sputtering target is deposited onto another sputtering target from which it is sputtered to produce a graded or mixed composition. Serial co-sputtering can be done continuously if the second target is periodically rotated in front of the first target and then in front of the substrate.[108]

Dual Arc and Sputtering Targets

By the proper rearrangement of magnets, a planar target can be used either for arc deposition or for sputtering. This arrangement allows the arc mode to be used for obtaining good adhesion of the film to the substrate using copious film ions. The film is then built-up in thickness using the sputtering mode thus avoiding the production of "macros."[109]–[112]

6.7.2 Target Materials

The purity of the sputtering target material should be as high as is needed to achieve the desired purity in the deposited material but not any higher, since the price of the target generally goes up rapidly with purity. In many cases, the supplier does not specify some impurities such as oxygen in the form of oxides, hydrogen such as found in chromium, etc. The target purity and allowable impurities should be specified in the initial purchase of the target material. At least there should be a purity certification from the supplier.

For some applications, such as submicron metallization of silicon with aluminum, extremely high purities are required and the allowable level may be very low for some materials. For example, the purity specified for aluminum may be 99.999% pure with <10 ppb (parts per billion) of uranium and thorium (radioactive materials).

As part of the specifications for a sputtering target the density of the target should be specified.* Generally the higher the density the better. Above about 96% density, porosity is primarily in the form of closed voids which open up during use. Below 96% many of the pores are interconnected

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*In developing an rf sputter deposited TiB_2 coating for a mercury switch, a powder pressed TiB_2 target was used because it could be obtained in a timely manner. It was known that the porous target would outgas but a functional coating was developed. When the process was ready to be transferred to production it was recognized that the production engineers would question the low density sputtering target so the development group determined that there was about 20% oxide in the sputter deposited TiB_2 film so the specifications were written to allow up to 20% oxide in the deposited film. The production engineers did not like the specifications so they obtained a very expensive high density TiB_2 target formed by CVD. The TiB_2 films from the high purity target performed no better than the oxide-contaminated films. Pure, high density targets are not always necessary but they are desirable for process reproducibility.

giving a porous material, and act as virtual leaks and contaminant sources. Porous targets can adsorb contaminants such as water and introduce a processing variable which may be difficult to control. For materials with poor thermal conductivity, thin targets are more easily cooled than thick targets thus reducing "hot-spots" and the tendency to fracture.

Targets which have been formed by vacuum melting (metals) or chemical vapor deposition (metals, compounds) are generally the most dense. Less dense targets are formed by sintering of powders in a gaseous or vacuum atmosphere with hot isostatic pressing (HIP) producing the most dense sintered product. Sintering sometimes produces a dense surface layer ("skin") but the underlying material may be less dense and this material becomes exposed with use. In some cases, it may be useful to specify the outgassing rate of the target as a function of temperature.

When using alloy or compound targets care must be taken that the target is of uniform composition, that is be homogeneous. This is particularly a problem when sputtering magnetic alloy material such as Co,Cr,Ta; Co,Ni,Cr,Ta; CoCr,Pt; Co,Fe,Tb; or Co,Cr,Ni,Pt where material distribution in the target is extremely important. In some cases, the composition of the deposited material may be different from that of the target material in a reproducible way due to preferential loss of material. Common examples of this problem are: ferroelectric films of $BaTiO_3$,[113] superconducting films such as $YBa_2Cu_3O_7$, and magnetic materials such as GbTbFe.[114] In the case of alloy deposition, the change in composition may be compensated for by changing the target composition so as to obtain the desired film composition.[115]

Second phase particles in the target can lead to the development of cones on the target surface during use due to the differing sputtering rates of the matrix material and the second phase particles. Also, second phase material in the target appears to influence the nucleation of the sputter-deposited material, possibly due to the sputtering of molecular species from the target.[116] Second phase precipitates can be detected using electrical conductivity measurements.[117]

In some cases, metal plates are rolled to a specific thickness to form the sputtering target. This can introduce rolling stresses and texturing that should be annealed before the plate is shaped to final dimensions. Annealing can cause grain growth which may be undesirable.

The grain size and orientation of the target material can affect the distribution of the sputtered material and the secondary electron emission from the target surface. The distribution of sputtered material is important

in obtaining uniform film thickness on the substrate especially if the target-substrate spacing is small. Variations in electron emission can lead to changes in the plasma density over the target surface. Grain orientation can be determined using X-ray diffraction techniques and grain size distribution can be determined using ultrasonic techniques.[117] The grain size and orientation can often be controlled during target fabrication.

6.7.3 Target Cooling, Backing Plates, and Bonding

Typically sputtering targets are in contact with a copper backing plate which contains the cooling channels for cooling the target and provides necessary rigidity. The cooling channels in the backing plate should be designed such that a vapor lock, caused by vaporization of the coolant at hot-spots, does not occur and prevent coolant flow. The coolant flow and temperature should be monitored and interlocked so that if there is a coolant failure, the target power will be turned off. In some configurations such as the S-gun, heating of the target causes it to expand and have good thermal contact with the backing plate. In other configurations, the target should be bonded to the backing plate.

Bonding can be done with high temperature techniques such as brazing, lower temperature techniques such as soldering, or low temperature techniques such as epoxy bonding using a low vapor pressure epoxy that can be silver-loaded to increase its thermal conductivity. This bond should be ultrasonically inspected in order to be sure that there are no unbonded areas ("holidays") which could give local hot spots. In many applications, heat transfer is a critical matter for the bonded targets.[118] Target fabricators often provide bonding services.

Targets are sometimes just clamped or bolted to the backing plate. This makes changing targets fairly easy but is often not a good approach, particularly if high powers are to be used, since mechanical contact generally provides poor thermal contact. Poor heat transfer allows the target to heat and expand. This makes bolting a problem. When the target is a brittle material, the stresses introduced can crack the target if the bolting is rigid. A possible solution is to use overlapping tiles with each tile individually bolted to the backing plate.

In some cases, the target is clamped in direct contact with the coolant. In this case the target must be rigid enough so that it does not warp under the pressure of the coolant. With this target design, the coolant

pressure should be regulated since a surge in coolant pressure can cause warping of the target.

6.7.4 Target Shielding

In DC diode non-magnetron sputtering, grounded shielding around the target is used to control the target area being bombarded and the shape of the electrical field near the target. The positioning of these shields is important to the erosion pattern especially near the edge of the target. Figure 4-2 shows the effect of field curvature on the bombardment and erosion of a target surface. Shields that are in close proximity to the target can be sputtered by high energy neutrals and introduce contamination into the deposited film. This source of contamination can be avoided by coating the shield with the same materials as the target. With use, flakes of film material may short the shield to the target causing arcing. The space between the shield and target should be periodically cleaned.

6.7.5 Target Specifications

Sputtering targets are sometimes fabricated in the sputtering plant,[119] but generally sputtering targets are purchased from an outside source. This means specifying the important target properties such as purity, density, mechanical properties, outgassing rate, geometry, etc. The ASTM (American Society for Testing and Materials) Committee F-1 is establishing standards for some sputtering targets. By 1996 the group has established standards for aluminum, gold, and refractory metal silicides. Often backing plates are bonded to targets by manufacturers and bonding requirement should be specified.

Sputtering target specifications can include:

Target material

- Dimensions and tolerances including flatness and surface finish of any sealing surface
- Purity along with allowable and non-allowable impurities to specific levels
- Grain size—particularly of compound materials
- Inclusions and second phase material
- Density

- Outgassing rate
- Fabrication method (required, preferred, not allowed)
- Residual stress

Backing plate

- Backing plate material, dimensions, surface finish, bolting configuration
- Bonding material and method
- Ultrasonic inspection of bonds for "holidays"

6.7.6 Target Surface Changes with Use

In some target designs the geometry of the target surface geometry changes with use. For example, in planar magnetron sputtering the target develops a "racetrack" depression on the surface. This changing geometry can affect the deposition rate, vapor flux distribution, and other deposition parameters such as the amount of reactive gas needed for reactive deposition in reactive sputter deposition. In some cases, portions of the target surface that are not being sputtered can become poisoned and arcing problems can increase with use. The surface morphology of the sputtering target may change with use producing a change in the flux pattern and a decreasing sputtering rate as the target changes geometry and becomes rough.

Roughening can be due to differences in sputtering rates of the crystallographic planes in a polycrystalline target, sputter-texturing of the surface (for example, cone formation), or surface recrystallization.[120] A target containing second phase material, such as inclusions, is more prone to roughening by forming cones on the surface than is a pure target. A dense cone morphology can be formed on a surface if a low sputtering yield material, such as carbon, is continually deposited on the target surface during sputtering (Fig. 2-15).[121][122] This carbon can come from hydrocarbon oil contamination or from carbon-containing vapor precursors. It has been found with an Al-Si-Cu target that the change of target surface morphology influences the microstructure[120] of the deposited film and it is proposed that the emission of dimers from the target surface is the reason.[123]

Some sputtering targets develop a "smut" of fine particles on the surface with use. If the smut occurs outside of the active sputtering region, it may be due to vapor phase nucleation and deposition of material sputtered from the target. If the smut develops on the active sputtering

region, it may be due to preferential sputtering combined with a high surface mobility of the un-sputtered constituent on the surface. The mobile species form islands on the target surface and they grow with time. A high target temperature contributes to this effect. To restore the target surface the smut can be wiped off.

Surface mobility can also cause the formation of nodules on the surface. For example, sputtering targets of indium-tin-oxide develop nodules on the surface with use. The origin of these nodules is uncertain and they must be machined off periodically.

6.7.7 Target Conditioning (Pre-Sputtering)

Generally the surface of the sputtering target is initially covered with a layer of oxide or contaminants and may be "pre-sputtered" before deposition begins. This pre-sputtering can be done with a shutter between the target and the substrate or by moving the substrate out of the deposition region while pre-sputtering of the target is being performed. When voltage-controlled power is first applied to a metal target, the current will be high and drop as the discharge comes to equilibrium.[124] The initially high current is due to the high secondary emission of the metal oxide as compared to the clean metal and the high density of the cold gas. As the oxide is removed from the surface and the gas heats up, the current density will fall. This target conditioning can introduce contaminant gas into the plasma. One advantage in using a lock-load deposition system is that the sputtering target can be maintained in a controlled environment at all times and pre-sputtering becomes less of a processing variable from run-to-run.

6.7.8 Target Power Supplies

Target power supplies may be DC, AC, pulsed DC, rf, DC + rf, etc. Continuous DC and AC power supplies are generally the most inexpensive. Unipolar pulsed DC can be generated by chopping (interrupting) the continuous DC. Bipolar DC requires a special power supply. Continuous DC and low-frequency AC power supplies require an arc suppression (quenching) circuitry to prevent voltage transients from feeding back into the power supply and blowing the diodes. Arc suppression can be done by cutting off the voltage or by reversing the voltage polarity for a short period of time.

The combining of rf with continuous DC has the advantage that the rf helps prevent arcing. When using rf with DC it is important that an rf choke be placed in the DC circuit to prevent rf from entering the DC power supply.

6.8 PROCESS MONITORING AND CONTROL

Sputter deposition has a number of process parameters that must be controlled in order to have a reproducible process and product. These include:

- *In situ* substrate cleaning (Sec. 12.10)
- Substrate temperature during deposition
- Gaseous contamination
- Sputtering rate
- Gas pressure
- Sputtering target voltage (which affects production of high energy reflected neutrals)
- Sputtering plasma uniformity
- System geometry
- Concurrent bombardment conditions on the growing film surface during deposition for reactive deposition
- Reactive gas density and uniformity
- Uniformity of plasma activation

6.8.1 Sputtering System

A good sputtering system should first be a good vacuum system. The vacuum capability is very important since it allows a reproducible plasma environment to be established. The plasma causes ion scrubbing of the system surfaces which desorbs contaminates into the plasma where they are activated and can react in a detrimental manner with the target or depositing material. Contamination in the system can be reduced by preconditioning the system using a plasma and then flushing the contamination from the system. Adequate gas throughput should be maintained during deposition to prevent the buildup of contamination in the deposition chamber. In rare cases, a static (non-pumped) system is used during

sputter deposition but this allows contamination to buildup in the deposition system.

Pumping speed in the vacuum chamber can be controlled by throttling the high vacuum valve or by the use of variable orifice conductance valves which may be servo controlled by a pressure gauge. A cryocondensation panel to pump water vapor or a sublimation pump (or getter sputter configuration) to pump reactive gases may be used in the deposition chamber in the presence of the plasma in order to reduce reactive contaminant species during the deposition process. In some cases, sputtering is performed with no reduction in pumping speed (i.e., high vacuum valve wide open). This has the advantage that it flushes contamination from the system but poses the requirement that the pumping system be able to handle high gas loads for an extended time.

6.8.2 Pressure

The properties of sputter deposited films can be very dependent on the gas pressure. For example, the film stress can vary dramatically with pressure.[16][97][98] If the pressure is low, the deposited film can have a high compressive stress while if the pressure is higher, the stress can be tensile. One method of controlling the film stress is to periodically cycle the pressure from a high to a low value during the deposition.[16] The pressure determines the thermalization of energetic particles in the system. Therefore it is very important to have precise pressure measurements from run-to-run. Vacuum gauges depending on ionization are not useful in sputtering since many stray ions are present in the system. Pressure gauging for sputtering is most often done using calibrated capacitance manometer-type or viscosity-type pressure gauges. In a sputtering system, pressure differentials can exist in the deposition chamber. These pressure differentials can be due to the gas injection manifolding, crowding in the deposition chamber, or position with relation to the pumping port. Therefore, gauge placement can be important for establishing position equivalency on the deposition fixture.

6.8.3 Gas Composition

Gas composition (partial pressure) can be an important variable in reactive sputter deposition.[92][125] Gas composition (partial pressures) can

be monitored using Residual Gas Analyzers (RGAs).[126] However, at sputtering plasma pressures, the RGAs are not very sensitive and will have to be differentially pumped or have a special ionizer construction in order to increase their sensitivity. The operation of the plasma can also affect the calibration of the RGA since ions are available without atoms having to be ionized in the RGA ionizer.

Gas composition can also be measured using optical emission spectroscopy[127] or optical absorption spectrometry. In optical emission spectrometry, the intensity of a characteristic emission from the plasma is monitored. By calibration, this intensity can be related to the density of the gas. Since the excitation/de-excitation intensity is dependent on the plasma properties it is important that a consistent geometry be used and this technique is often used in a comparative manner to insure process reproducibility. Optical adsorption spectrometry utilizes the attenuation of an optical beam to determine gas or vapor density over a path through the deposition chamber.

6.8.4 Gas Flow

In reactive sputter deposition the gas (mass) flow is an important processing variable and in non-reactive deposition, gas flow is important in sweeping contaminants from the processing chamber. A typical gas flow rate is 200 sccm or higher. Gas flow rates are measured by flow meters (Sec. 4.6.1). Flow meters generally operate by measuring the thermal conductivity of the gas and therefore the calibration varies with the gas species. Flow meters should be calibrated periodically.

In some cases, vapors are introduced into the deposition chamber by vaporization of a liquid outside the system in a vaporization chamber. This vapor can then be transported through heated lines to the deposition system often using a carrier gas. The vapor or vapor/gas flow can be measured by a flow meter or the liquid precursor can be vaporized and accurately introduced into the vaporization chamber using a peristaltic pump. Care must be taken with this system in that the peristaltic pump can introduce a periodic variation in the partial pressure of the vapor in the deposition chamber.

6.8.5 Target Power and Voltage

Reproducible sputtering parameters mean monitoring the target power (watts/cm^2) and voltage. In the case of rf sputtering, the reflected power from the target is measured and controlled by the impedance matching circuit. DC power supplies should have an arc suppression circuit which reacts to a current surge or a voltage drop. Arc suppression can be accomplished by shutting off the power or by providing a positive potential to counteract the arc. In reactive deposition there can be a hysteresis on target power due to reaction of the target surface with the reactive gas.

6.8.6 Plasma Properties

Typically plasma properties of ion and electron density and temperature are not monitored. A reproducible plasma is established by having a constant geometry, gas pressure, gas composition, and target voltage and current (power). However Atomic Adsorption Spectrometry (AAS) can be used to determine the flux of sputtered particle leaving the target surface (Sec. 6.8.8).

6.8.7 Substrate Temperature

Thermocouples embedded in the substrate fixture often provide a poor indication of the substrate temperature since the substrate often has poor thermal contact to the fixture. In some cases thermocouples can be embedded in or attached directly to the substrate material. Infrared pyrometers allow the determination of the temperature if the surface emissivity and adsorption in the optics is constant and known.[128] When looking at a rotating fixture some IR pyrometers can be set to only indicate the maximum temperature that it sees.

Passive temperature monitors can be used to determine the maximum temperature a substrate has reached in processing. Passive temperature monitors involve color changes, phase changes (e.g., melting of indium), or crystallization of amorphous materials.[129]

6.8.8 Sputter Deposition Rate

It is difficult to use quartz crystal deposition rate monitors with sputtering because of the close spacing and large areas. Deposition rate monitors using optical atomic adsorption spectrometry (AAS) of the vapor are quite amenable to use in a plasma.[130]–[132] In atomic adsorption spectroscopy a specific wavelength of light, that is absorbed by the vapor species, is transmitted through the vapor flux and compared to a reference value. Typically the light source is a hollow cathode lamp whose cathode is made of the same material as that to be measured. The light source emits an emission spectrum of radiation and the bandpass filter (or monochrometer) eliminates all radiation but the wavelength of interest. For example, copper vapor adsorbs strongly at 324.7 and 327.4 nm. A simple single-beam atomic adsorption deposition rate monitor is shown in Fig. 6-13.

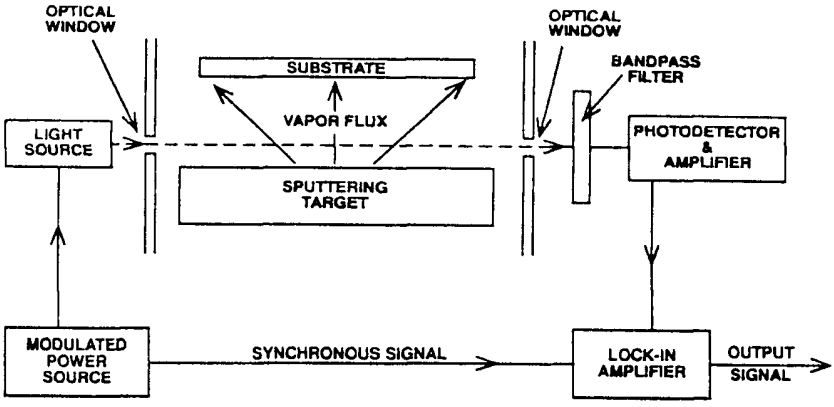


Figure 6-13. Atomic Adsorption Spectrometer (AAS) sputtering/deposition rate monitor.

Calibration is necessary to relate the adsorption to the actual deposition rate. By using a feedback loop to the vaporization source the vaporization rate can be controlled. Detection and control of deposition rates as low as 0.1 monolayers per second have been reported. The technique is most sensitive at low flux densities (<10Å/sec). By using several wavelengths, several vapor species can be monitored at the same time.

The AAS rate monitoring technique has the advantage that it is non-intrusive, can be used in small volumes, in closely-spaced regions and close to a surface. Problems with using the atomic adsorption techniques are with calibration drift, changing transmission of the optical windows, light source instability, optical alignment shifts, and detector drift. These problems can be mostly avoided by using a two-beam ratio detection system and periodic calibration during the deposition.

6.9 CONTAMINATION DUE TO SPUTTERING

6.9.1 Contamination from Desorption

Plasmas in contact with surfaces are very effective in desorbing adsorbed species by ion scrubbing (Sec. 12.10).

6.9.2 Target-Related Contamination

The sputtering target can be a source of gaseous, vapor, or particulate contamination in the deposition system by outgassing if it is porous. Sputtering targets have been shown to generate particulates in the deposition chamber. These particulates can come from second phase particles in the target that are stressed and fracture as they are exposed. For example in W-10%Ti (W-10Ti) targets, the particle generation is a function of the amount of second phase material formed during fabrication.[133] Particle generation from W-10Ti targets is decreased by using low-temperature fabrication techniques which reduces the amount and size of the second phase material. Particles may also be formed from pressed powder targets as the particles are loosened by erosion. The particle generation is inversely related to the target density. In many cases target materials may be rolled or forged after fabrication. This can introduce stresses and texturing in the target, that produce fracture in the target surface that contribute to particle generation. To avoid these problems the target may be ground to flatness and the target shaped using Electric Discharge Machining (EDM).

In DC diode sputtering, the target fixturing and shielding can be sputtered by the high energy neutrals formed by charge exchange processes. These high energy neutrals are not affected by the electric fields.

In some cases the fixturing can be coated with the target material to prevent contamination by sputtering of the fixture/shield.

6.9.3 Contamination from Arcing

Arcing on surfaces, with associated particle generation, can occur on the target surface or other surfaces in the deposition chamber due to electrical potential variations over surfaces and between the surfaces and the plasma. This is particularly a problem when depositing electrically-insulating films by reactive deposition. This arcing can be reduced by using a combination of DC and rf potentials on the target, using pulsed DC sputtering and by having arc-suppression circuits in the power supplies.

6.9.4 Contamination from Wear Particles

Wear particles can be generated from fixturing and tooling in the deposition chamber. Fixturing and tooling should be designed so that wear particles do not fall on the substrates. System vibration increases the particle generation.[134]

6.9.5 Vapor Phase Nucleation

During high-rate sputtering over long periods of time, ultrafine particles formed by gas phase nucleation can be produced (Sec. 5.12).[135]–[140] Particles in a plasma assume a negative charge with respect to the plasma and any surfaces in contact with the plasma, so the particles are suspended in the plasma particularly near the edge. The behavior of these particles has been studied using *in situ* laser scattering techniques. When the plasma is extinguished these particles settle out on surfaces. In order to minimize particle settling, the plasma should be extinguished by increasing the pump throughput by opening the throttle valve and sweeping the particles into the pumping system before the discharge is extinguished.

6.9.6 Contamination from Processing Gases

The gases introduced into the plasma system can contain impurities. The first step in eliminating the impurities is to specify the desired gas

purity from the supplier. Inert gases can be purified by passing them over a hot bed of reactive material such as titanium or uranium. Commercial gas purifiers are available that can supply up to 5×10^3 sccs. Moisture can be removed from the gas stream by using cold zeolite traps. Gas purifiers should be routinely used on all sputtering systems in order to ensure a reproducible processing gas. Distribution of the gases should be in non-contaminating tubing such as Teflon™ or stainless steel. For critical applications, the stainless steel tubing can be electopolished and a passive oxide formed. Particulates in the gas line can be eliminated by filtration near the point-of-use.

6.9.7 Contamination from Deposited Film Material

When a sputtering system is used for a long time or high volumes of materials are sputtered, the film that builds up on the non-removable surfaces in the system increases the surface area and porosity. This increases the amount of vapor contamination that can be adsorbed and retained on the surface. This source of contamination can be reduced by periodic cleaning and controlling the availability of water vapor during process cycling either by using a load-lock system or by using heated system walls when the system is opened to the ambient (Sec.3.12.2).

The film buildup can also flake-off giving particulate contamination in the deposition system.[141] Fixturing should be positioned such that particulates that are formed do not fall on the substrate surface. The effects of contamination from this source can be minimized by having the substrate facing downward or sideways during deposition. The system should be periodically "vacuumed" using a HEPA-filtered vacuum cleaner. The use of a "soft-rough" and a "soft-vent" valve minimizes "stirring-up" the particulate contamination in the system.

6.10 ADVANTAGES AND DISADVANTAGES OF SPUTTER DEPOSITION

Advantages in some cases:

- Any material can be sputtered and deposited—e.g., element, alloy or compound.

- The sputtering target provides a stable, long lived vaporization source.
- Vaporization is from a solid surface and can be up, down or sideways.
- In some configurations, the sputtering target can provide a large area vaporization source.
- In some configurations the sputtering target can provide specific vaporization geometries—e.g., line source from planar magnetron sputtering source.
- The sputtering target can be made conformal to a substrate surface such as a cone or sphere.
- Sputtering conditions can easily be reproduced from run-to-run.
- There is little radiant heating in the system compared to vacuum evaporation.
- In reactive deposition, the reactive species can be activated in a plasma.
- When using chemical vapor precursors, the molecules can be dissociated or partially dissociated in the plasma.
- Utilization of sputtered material can be high.
- *In situ* surface preparation is easily incorporated into the processing.

Disadvantages in some cases:

- In many sputtering configurations the ejection sputter pattern is non-uniform and special fixturing, tooling or source design must be used to deposit films with uniform properties.
- Most of the sputtering energy goes into heat in the target and the targets must be cooled.
- Sputter vaporization rates are low compared to those that can be achieved by thermal vaporization.
- Sputtering is not energy efficient.
- Sputtering targets are often expensive.
- Sputter targets, particularly those of insulators, may be fragile and easily broken in handling or by non-uniform heating.
- Utilization of the target material may be low.

- Substrate heating from electron bombardment can be high in some configurations.
- Substrates and films may be bombarded by short wavelength radiation and high energy particles that are detrimental to their performance.
- Contaminants on surfaces in the deposition chamber are easily desorbed in a plasma-based sputtering due to heating and ion scrubbing.
- Gaseous contaminants are "activated" in plasma-based sputtering and become more effective in contaminating the deposited film.
- When using chemical vapor precursors the molecules can be dissociated or partially dissociated in the plasma to generate "soot."
- High energy reflected neutrals in low-pressure and vacuum sputtering can be an important, but often uncontrolled, process variable.

6.11 SOME APPLICATIONS OF SPUTTER DEPOSITION

Some applications of sputter deposited films are:[142]

- Single and multilayer metal conductor films for microelectronics and semiconductor devices, e.g. Al, Mo, Mo/Au, Ta, Ta/Au, Ti, Ti/Au, Ti/Pd/Au, Ti/Pd/Cu/Au, Cr, Cr/Au, Cr/Pd/Au, Ni-Cr, W, W-Ti/Au, W/Au
- Compound conductor films for semiconductor electrodes, e.g., WSi_2, $TaSi_2$, $MoSi_2$, PtSi
- Barrier layers for semiconductor metallization, e.g., TiN, W-Ti
- Magnetic films for recording, e.g. Fe-Al-Si, Co-Nb-Zr, Co-Cr, Fe-Ni-Mo, Fe-Si, Co-Ni-Cr, Co-Ni-Si
- Optical coatings—metallic (reflective, partially reflective), e.g. Cr, Al, Ag
- Optical coatings—dielectric (antireflective and selective reflective), e.g., MgO, TiO_2, ZrO_2

- Transparent electrical conductors, e.g., InO_2, SnO_2, In-Sn-O (ITO)
- Electrically conductive compounds, e.g., Cr_2O_3, RuO_2
- Transparent gas/vapor permeation barriers, e.g., SiO_{2-x}, Al_2O_3
- Diffraction gratings, e.g. C/W
- Photomasks, e.g., Cr, Mo, W
- Wear and erosion resistant (tool coatings), e.g., TiN, (Ti-Al)N, Ti(C-N), CrN, Al_2O_3, TiB_2
- Decorative, e.g., Cr, Cr alloys, copper-based alloys (gold colored)
- Decorative and wear-resistant, e.g., TiC, TiN, ZrN, Ti(C-N), (Ti-Al)N, Cr, Ni-Cr, CrN, HfN
- Dry lubricant films—electrically nonconductive, e.g., MoS_2
- Dry lubricant films—electrically conductive, e.g., WSe_2, $MoSe_2$
- Freestanding structures[143]

6.12 SUMMARY

Sputtering is generally more expensive than vacuum evaporation and the choice of the use of sputter deposition generally involves utilizing one or more of its advantages such as being a long-term source of vapor, allowing a close source-substrate spacing, low substrate heating or providing reactive deposition conditions.

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7

Arc Vapor Deposition

7.1 INTRODUCTION

Arc vapor deposition is a PVD technique which uses the vaporization from an electrode under arcing conditions as a source of vaporized material.[1]–[4] Arcing conditions consist of a high-current low-voltage electrical current passing through a gas or a vapor of the electrode material. The arc voltage only has to be near the ionization potential of the gas or vapor (>25 volts). Ion bombardment at the cathode and electron bombardment at the anode heat the electrodes. Most of the ejected material is thermally evaporated but some is ejected as molten droplets or solid particles from the cathode. A high percentage of the vaporized atoms are ionized in the arc vaporization process. The arc can be established between closely spaced electrodes in a good vacuum (vacuum arc) by vaporizing some of the electrode material, or between electrodes in a low-pressure or high-pressure gaseous environment (gaseous arc). High pressure gaseous arcs are not used in PVD processing but are used in processes such as plasma spraying, arc welding, and electrospark plating.[5] In PVD processing, arc vaporization can be considered a unique vaporization source along with thermal vaporization and sputtering.

Arc vaporization was first reported by Robert Hare in 1839 and has been of concern in electrical contact engineering,[6] arc melting of alloys,[7] as a source of contamination in fusion reactor technology,[8][9] as a source of contamination in PVD processes using high voltages as well as a vaporization source for PVD film deposition. Early use of vacuum arc deposition of thin film was to deposit carbon[10] and metal[11] films. Arc-deposited carbon has long been used as a replication film in electron microscopy. Exploding wires (Sec. 5.3.5) are a type of arc discharge.

7.2 ARCS

7.2.1 Vacuum Arcs

Arc vaporization in a low pressure vacuum occurs when a high current-density, low voltage electric current passes between slightly separated electrodes in a vacuum, vaporizing the electrode surfaces and forming a plasma of the vaporized material between the electrodes as shown in the Fig. 7-1. In order to initiate the arc, usually the electrodes are touched then separated by a small distance. On the cathode a "cathode spot" is formed that has a current density of 10^4–10^6 A/cm^2.[12] This current density causes arc erosion by melting and vaporization and by the ejection of molten or solid particles. On the anode the current density is much less but can be sufficient to melt and evaporate the anode. A high percentage of the vaporized material is ionized in the arc and the ions are often multiply charged.[13]

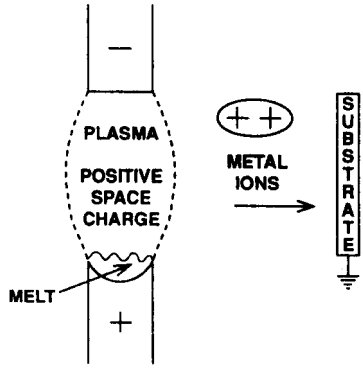


Figure 7-1. Vacuum arc.

Since the ions move more slowly than the electrons, a positive space charge is generated in the plasma and positive ions are accelerated away from the plasma to energies that are much higher than thermal energies, typically 50–150 eV. This means that the deposition of the electrode material in vacuum where there is no thermalization, is accompanied by concurrent bombardment by the high-energy "film ions." The ions in the vacuum arc can be extracted and accelerated to high energies as a metal ion source.[14]–[16] Carbon ions (500 eV) from a vacuum arc source have been used to deposit hydrogen-free diamond-like carbon films.[17][18]

7.2.2 Gaseous Arcs

The gaseous arc involves utilizing a gaseous environment ranging from a few mTorr to atmospheric pressure or even higher. When using a gaseous arc for film deposition, the gas pressure is kept low to prevent gas phase nucleation of the vaporized material and allow the acceleration of ions from the plasma without collision and thermalization. In the gaseous arc, gaseous atoms as well as atoms from the electrodes are ionized and sustain the discharge. This allows the arcing electrodes to be more widely separated than in the vacuum arc.

The potential distribution in the interelectrode region of a gaseous arc depends on the voltage, gas pressure, and total current. The components of the potential drop are: cathode fall, plasma potential, and the anode fall. There can be appreciable space charge effects on the potential at both the cathode and the anode.

The gas that is used in gaseous arc deposition can be an inert gas such as argon if the deposition of an elemental material is desired or can be a reactive gas or a mixture of reactive and inert gas if the deposition of a compound material (reactive deposition) is desired.

7.2.3 Anodic Arcs

In an arc discharge, if the anode is molten, material evaporates from the molten anode surface into the arc and the source is called an anodic arc source.[19]–[25] This type of arc is sometimes called a distributed arc since the current density is much lower on the anode than in the cathode spot (~10 A/cm^2 vs 10^4–10^6 A/cm^2). The anodic arc has the advantage that molten globules are not formed. Since the anode is molten there will be

preferential vaporization of constituents of an alloy electrode so deposition of alloy materials and multi-component compound materials can be difficult using the anodic arc. The degree of ionization of the vaporized electrode material in the anodic arc is generally less than in the cathodic arc and the ions are typically singly charged.

Anodic arcs can be categorized as to the source of electrons.[26] The electrons can arise from a heated thermoelectron emitting surface,[27]–[30] a hot or cold hollow cathode,[31]–[35] or an arc cathode.[23][36]–[38] By bending the electron beam in a magnetic field, the vaporized material may be kept from impinging on the electron source. Commercial sources for anodic arc deposition are available.

An example of using the anodic arc is the deposition of adherent silver films on beryllium using a hot hollow cathode electron source with magnetic beam-bending as shown in Fig. 7-2. By applying a high negative DC bias on the beryllium substrate, the beryllium is sputter-cleaned by the silver and gaseous ions then by reducing the bias, an adherent silver film is formed.[39]

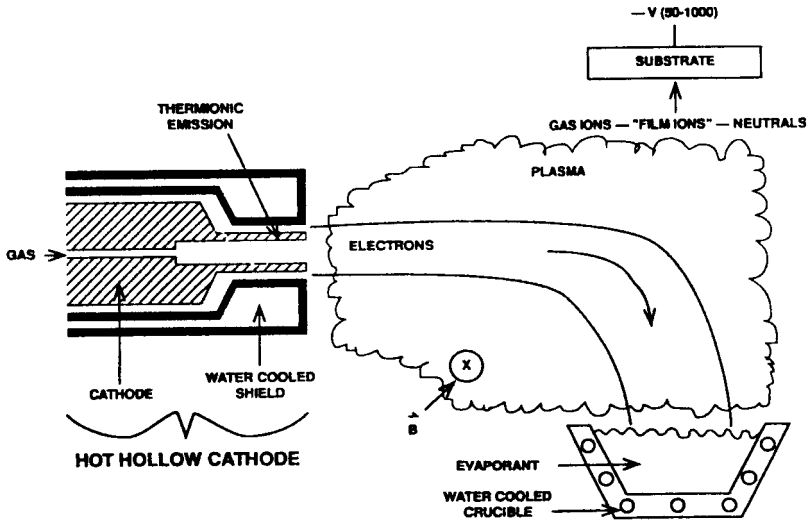


Figure 7-2. Anodic arc deposition of silver on beryllium (adapted from Ref 39).

7.2.4 Cathodic Arcs

If the vaporization primarily occurs from the cathode surface by arc erosion the system is called a continuous cathodic arc source.[40]–[42] The cathode can be molten or solid with a water cooled solid cathode ("cold cathode"). The cold cathode source is the most common cathodic arc source for film deposition. In order for a stable arc to form there must be a minimum current passing through the arc. Minimum arc currents vary from about 50–10A for low melting point materials such as copper and titanium to 300–400A for refractory materials such as tungsten. Most of the arc voltage drop will occur near the cathode surface. The arc voltage can be from about 15 volts to 100 volts depending on the ease of electron motion from the cathode to the anode (i.e., cathode design). The energy dissipation in the arc is about (very approximate):[41]

Heat	34%
Electron emission	21%
Evaporation (atoms and macros)	3%
Ionization (single & multiple)	7%
Energy to ions	23%
Energy to electrons	10%

Problems with the cathodic arc deposition technique include stabilization and movement of the arc on the solid surface and the formation of molten micron-sized "globules" (or "macros") of the ejected material from the solid surface.[43][44] Macros are not formed if the cathode is molten. If the arc is allowed to move randomly over the surface the arc source is called a random arc source. If the arc is confined and caused to move over the surface in a particular path the source is called a "steered arc" source. There are a number of different steered arc source designs using magnetic fields to steer the arc. Steered arc sources generally produce fewer macros than random arc sources.

The high-density electron current on the solid arc-cathode forms a cathode spot which generally moves over the surface until it is extinguished. The electron current in the spot is from 30–300 amps and the current density in the spot can be greater than 10^4 A/cm^2. If the current density is very high, the arc will break up into two or more spots (arcs). During random motion, the cathode spot may attach to a surface

protuberance or a region of high electron emission, such as a oxide inclusion, until it vaporizes the region.

Arc movement on the cathode is affected by the gas composition and pressure, cathode material and impurities and the presence of magnetic fields. When there is no magnetic field, the arc tends to move in a completely random manner. If the cathode is a disk, then statistically the arc is mostly in the center and the erosion will mostly be in the center of the disk. If there is a weak magnetic field normal to the cathode surface, the arc will trace a random but spiral path on the surface. If a stronger magnetic field is present, the arc movement will be determined by the angle of the magnetic field with the surface. In the "arched field" design, the spot will move along the surface where the magnetic field normal to the surface is zero—much as the dense plasma region ("racetrack") in magnetron sputtering. This design configuration is easily formed on a planar surface or a surface of revolution such as a cylinder. One commercial supplier provides cathodes which can be used either as cathodic arc sources or as magnetron sputtering sources with small changes in the magnetic field configuration.[45][46]

7.2.5 "Macros"

Macros are formed by ablation of molten or solid particles by thermal shock and hydrodynamic effects in the molten spot on a solid surface. Macros are not formed from molten anodic or cathodic surfaces. The number and size of macros produced from the solid arc cathode surface depends on the melting point and vapor pressure of the cathode material and the arc movement. Large (tens of microns diameter) macros are formed with low melting point materials and slow arc movement while small macros (< 1 micron) are formed with high melting point materials and rapid arc movement. The molten globules can represent a few to many percent of the material ejected from the cathode. For example, in arc deposition of ZrN from a zirconium cathode, it is estimated that 1% of the deposited zirconium is in the form of globules. The distribution of globule emission is non-isotropic with the maximum number being found at angles greater than 60° from the normal to the surface. The globules have a velocity of 250–350 m/sec. Material may thermally evaporate from the ejected molten globules and many of the neutral atoms found in arc vaporization are thought to be produced by thermal evaporation from the ejected globules. This effect can cause the composition of the

deposited film to vary with thickness and position when depositing an alloy material.[47]

The globules can be "filtered" from the arc using various means such as the "plasma duct."[48]–[50] Another approach to reducing the number of macros is to have the vapor and macros pass through a high density plasma to further evaporate the macros.[51] At high plasma densities (high enthalpy), ions and electrons recombine on the surface of particles and can be a significant source of heat input. Heating by recombination is a significant factor in melting particles in plasma spraying.[52]

The number and size of the globules increases with lower melting point materials, high cathode currents, and high cathode temperatures. The number of macros that deposit on the substrate can be minimized by decreasing the arc current, increasing the source-substrate distance, increasing gas pressure and by using a co-axial magnetic field to increase the plasma density.[51][53][54] In reactive deposition, the number of macros decreases with the partial pressure of the reactive gas—probably due to the reactive gases reacting with the target surface producing a more refractory material.

7.2.6 Arc Plasma Chemistry

Enthalpy is the sum of the internal energy (heat content) of a system. The enthalpy of an arc depends on the particle density and degree of ionization. The presence of a high density of energetic electron in the plasma makes the arc plasma a rich region for activation of chemical species. This activation dissociates chemical species, creates new chemical species, and produces ions that can be accelerated under an applied electric field. This is important in reactive film deposition processes and ion plating.

7.2.7 Postvaporization Ionization

In some cases, particularly when using anodic arcs, it may be desirable to increase the ionization of the vaporized film species. This can be done by establishing an auxiliary plasma between the arc source and the substrate or by using an axial magnetic field to increase the electron path length and ionizing collision probability.[51][53][54]

7.3 ARC SOURCE CONFIGURATIONS

7.3.1 Cathodic Arc Sources

There have been a number of designs of cathodic arc sources. Each source has to have some way of initiating the arc and a configuration that re-ignites the arc when it is extinguished.

Arc Initiation

The arc can be initiated by touching and separating the electrodes, using a high voltage "trigger arc," laser ionization or some other technique that forms ions and electrons in a path between the electrodes. Typically a trigger arc is obtained from a high voltage on an auxiliary electrode near the cathode surface causing the arc to form. When an arc is extinguished, the inductance in the arc power supply gives a voltage spike which re-ignites the arc.

Random Arc Sources

The original patent on the non-magnetic cathodic random arc source was by Sablev.[55] Random arc sources are generally round and either surrounded by a shield separated from the target or an insulator in contact with the target (passive arc confinement) as shown in Fig. 7-3. As the arc enters the space between the target and the shield or moves onto the surface of the insulator, it is extinguished. The anode can be either the chamber walls or a separate surface in the vacuum system.

A weak magnetic field can be used to keep the arc on the surface without really controlling the arc motion.[56] This is classed as a random arc configuration. The magnetic field can be normal to the surface and axially inhomogenous, in which case the arc will execute a circular path around the axis of the magnetic field.

Steered Arc Sources

In the steered arc source the arc is confined to the surface by a magnetic field and caused to move in a specific path and with a greater

velocity than with the random arc. Usually the magnetic field has an arched configuration that closes on itself as shown in Fig. 7-4. The magnetic field can be established using elecromagnets or permanent magnets. Permanent magnets can be physically moved to steer the arc.

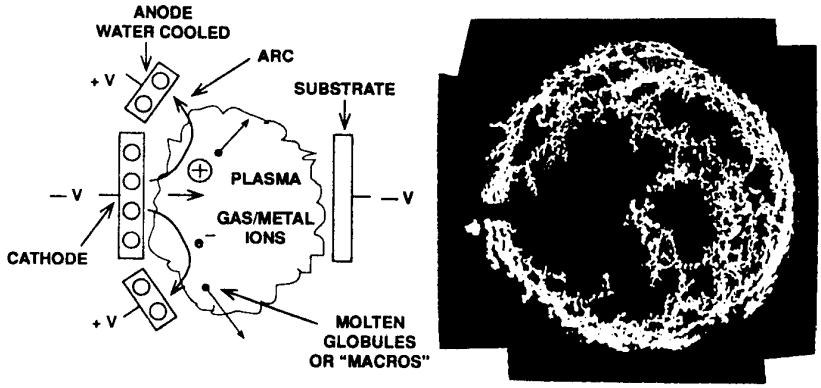


Figure 7-3. Random cathodic arc sources and a picture of the arc movement over the surface.

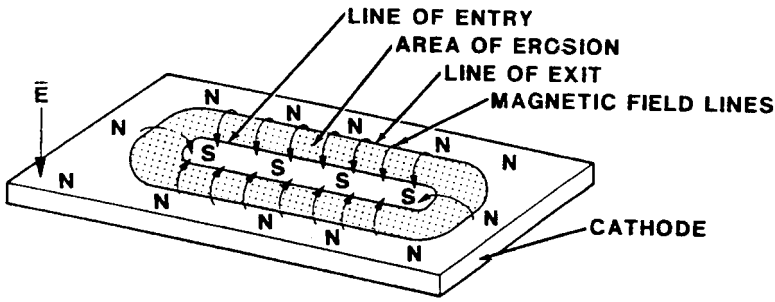


Figure 7-4. Steered cathodic arc source.

The arched field configuration is very similar to the planar magnetron sputtering configuration and the cathode can be converted from an arcing mode to a sputtering mode by changes in the magnetic field configuration.[45][46] This allows the initial deposition to be performed using arc vaporization to obtain good adhesion and the film thickness built up using magnetron sputter deposition to avoid the production of macros. This is called the Arc-Bonded-Sputtering (ABS™) process.[45][46][57]

Pulsed Arc Sources

Pulsed arcs can be made by making and breaking the arc circuit by repetitively touching the arcing surfaces or by using a pulsed DC power supply. Pulsing is usually done in vacuum and usually does not require active cooling. This is the type of source that is used in some metal ion sources.[18][58]

"Filtered Arcs"

The macros can be removed from the arc plasma ("filtered") by several techniques. The most common technique is the use of a plasma duct either in the form of a torodial section as shown in Fig. 7-5[59]–[61] or a bent "knee" configuration.[62] In the duct, the plasma is bent out-of-line-of-sight of the cathodic arc source by a magnetic field. The macros are deposited on the walls and only charged film-ions get to the substrate. Typically, the deposition rate is cut by about one-half when using the plasma duct. The deflected beam can be rastered over the substrate surface to give large-area deposition.[62] Deposition rates of amorphous carbon (a-C) of up to 16,000 Å/min over a 2 centimeter diameter spot have been reported.[62] By changing the substrate bias during deposition the properties of the carbon film can be controlled.

"Self-Sputtering" Sources

The sputtering process does not generate macros. "Self-sputtering" is when a high energy atom or ion of the target material bombards a sputtering target and sputters the target material. This provides an ideal match of particle masses to give sputtering (Sec. 6.2.1). The cathodic arc source provides copious ionized metal ions that can be accelerated to

sputter a target. Sanders used a cathodic arc source to vaporize and ionize metal ions, a magnetic field for post vaporization ionization to increase the ion density, and self-sputtering to vaporize the sputtering target material to be deposited.[63] This arc-vaporization/sputter-deposition technique eliminates the problem of macros hitting the substrate surface.

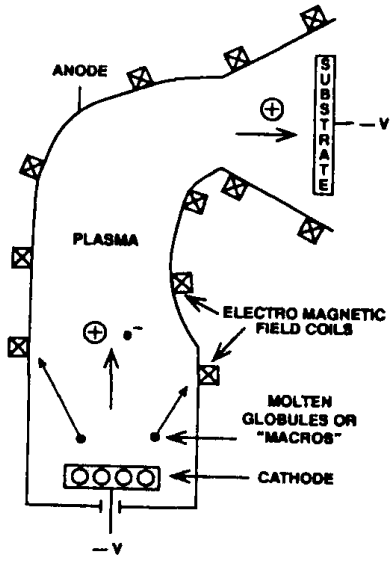


Figure 7-5. "Filtered arc" source using a plasma duct.

7.3.2 Anodic Arc Sources

Anodic arc sources are basically evaporation sources heated by low-voltage high-current unfocused electron beams[36]–[38][64] (Sec. 5.3.1). The electron beam can be bent by a magnetic field so that the emission source is out-of-line-of-sight of the evaporation source as shown in Fig. 7-2 or it can be in the line-of-sight. The electrons can be made to spiral in a magnetic field so as to increase the postvaporization ionization probability of the evaporated material. Figure 7-6 shows some anodic arc source configurations.

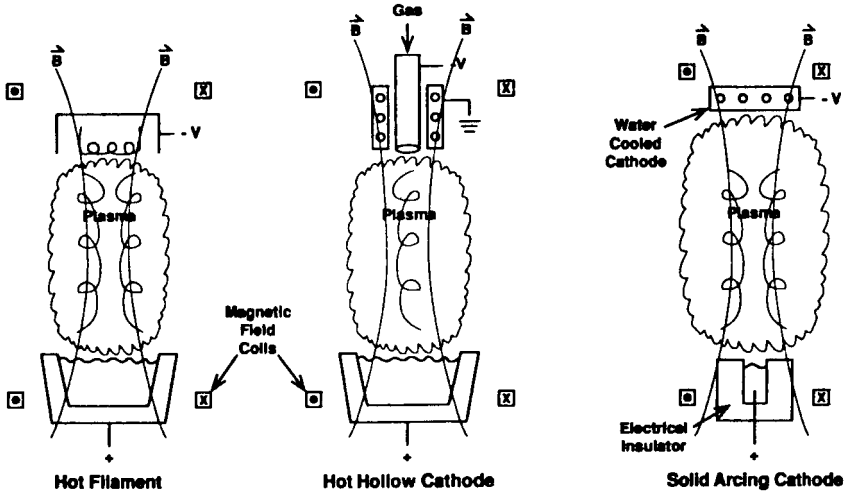


Figure 7-6. Anodic arc sources.

7.4 REACTIVE ARC DEPOSITION

In reactive arc deposition, the reactive gas is activated in the arc plasma. Usually the deposition is done in an ion plating mode, i.e., ions of both the film material and the reactive gas are accelerated to the substrate.[46][47][57] Since ions do not play a role in the vaporization of the electrodes, there is no need for an inert gas except for sputter cleaning of the substrate. A partial pressure of inert gas may be needed to help sustain the arc if the composition of the deposited film is graded by controlling the availability of the reactive gas.

7.5 ARC MATERIALS

Cathodes for cathodic arcing should be made from fully dense material. Pressed powder targets should be avoided since they do not give stable arcing and particles are ejected from the arcing surface. The molten material for anodic arcing is usually contained in a crucible in much the same way as for thermal evaporation (Sec. 5.3.1).

7.6 ARC VAPOR DEPOSITION SYSTEM

Arc vapor deposition does not have any special vacuum requirements. In reactive arc deposition, gas flow control must be established and controlled in much the same way as for reactive sputter deposition (Sec. 6.8). In the cathodic arc deposition from a cooled cathode, coolant flow and temperature sensors should be used in the cathode coolant circuit.

Usually in arc vapor deposition, the deposition chambers are large to allow the fixtures to be placed well away from the arc source. This is similar to the vacuum deposition chamber shown in Fig. 5-9. When using a cathodic arc deposition, often several sources are positioned in the chamber. Another cathodic arc configuration uses a centrally positioned post as the cathodic electrode. When using such a large chamber, it means that large areas will collect excess deposited film and have to be cleaned.

7.6.1 Power Supplies

Arcing uses low-voltage (100 volts) high-current (hundreds of amperes) power supplies much like arc-welding power supplies. The power supply must have a high inductance in order to form the high voltage pulse necessary to re-ignite an arc when an arc is quenched. In addition to the arc supply, a high voltage (to 1000 volts) DC bias power supply is often needed to allow sputter cleaning and heating of the parts in the chamber. The bias is typically reduced to 50–100 volts during deposition.

7.6.2 Fixtures

Arc vapor deposition often involves coating three-dimensional objects and rotatable fixtures are necessary that allow deposition over the whole surface with a uniform angle-of-incidence of the depositing vapor flux. Often the fixture is biased to some voltage to allow sputter cleaning and energetic bombardment of the growing film.

In some designs, the arc sources are mounted on the chamber walls and in other designs the arc source is a post in the center of the chamber. The positioning of the arc source(s) affects the design of the fixtures and tooling used to hold and move the substrates (Fig. 3-12).

7.7 PROCESS MONITORING AND CONTROL

Most current application of arc vapor deposition do not require stringent film thickness control. The amount of deposited film is determined by the process parameters, fixture configuration and deposition time. Often the substrates to be coated are heated in the deposition system. For example, tool bits are heated to 300–400°C. This can be done with radiant heaters or by ion bombardment during sputter cleaning. The temperature is monitored using a maximum-reading infrared optical pyrometer.

In arc deposition, gas pressure control is generally not as critical as in sputter deposition and the gas pressure is monitored in the same manner as for sputter deposition (Sec. 6.8).

7.8 CONTAMINATION DUE TO ARC VAPORIZATION

The most common contaminants are particulates generated during cold cathodic arc deposition. These can be molten globules when ejected from the cathode or they may be solid particles such as those ejected from carbon or pressed powder targets.

7.9 ADVANTAGES AND DISADVANTAGES OF ARC VAPOR DEPOSITION

7.9.1 Advantages

Arc vaporization provides a higher vaporization rate than does sputtering but not as high as can be obtained by thermal evaporation. Vaporization from solid surfaces allows cathodic arc sources to be mounted in any configuration. The production of copious gaseous and film ions provides a high flux of ions for sputter cleaning and modifying film properties by concurrent bombardment during deposition. The low voltage power supplies used are attractive from a safety standpoint.

7.9.2 Disadvantages

The production of macros can be a determining factor in some applications.

7.10 SOME APPLICATIONS OF ARC VAPOR DEPOSITION

Both anodic and cathodic arc vaporization are widely used to deposit hard and wear resistant coatings both for decorative and functional applications.[3][65] Typically, these coatings are a few microns in thickness. Many of the arc deposition processes are used in the ion plating mode, i.e., with concurrent energetic particle bombardment during film deposition which affects the film properties.[66] Cathodic arc deposition is the most widely used arc technique when vaporizing alloy electrodes such as Ti-Al.

- Deposition of TiN, ZrN, TiC, Ti(C,N), (Ti,Al)N, CrN hard coatings on tools, injection molds
- Deposition of TiN & Zr(CN)(gold-yellow), ZrN (brass) and TiC (black) and Ti(N,C) (rose, violet, etc.) for decorative wear-resistant coatings
- Deposition of oxides for optical coatings (anodic arc)
- Deposition of adherent metal coatings
- Deposition of amorphous-carbon (a-C) and diamond-like-carbon (DLC) coatings (cathodic arc)
- As an adherent basecoat on which the balance of the coating is formed by sputter deposition or thermal evaporation (cathodic arc)

7.11 SUMMARY

Arc vaporization, particularly cathodic arc vaporization, provides a means for forming copious amounts of film-ions and reactive gas ions. The arc vaporization source is often used in an ion plating mode, i.e,. with a substrate potential to accelerate the film to the substrate surface. The energetic film ions can be used to sputter clean the substrate surface,

implant film atoms into the substrate surface and then modify the film properties by concurrent bombardment. The technique can be used to obtain very adherent and dense films. Arc vaporization can provide a higher vaporization rate than sputtering but cannot achieve the vaporization rates obtained by thermal vaporization. By using steered arc sources, special vaporization configurations such as an elongated racetrack can be used. The problem of the generation of macros has been dealt with by a number of designs and processing procedures. Activity in this area continues.

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8

Ion Plating and Ion Beam Assisted Deposition

8.1 INTRODUCTION

"Ion Plating" (or Ion Assisted Deposition—IAD) is a generic term applied to atomistic film deposition (PVD) processes in which the substrate surface and the growing film are subjected to a continuous or periodic bombardment by a flux of energetic atomic-sized particles sufficient to cause changes in the film formation process and the properties of the deposited film. This definition does not specify the source of the depositing film material, the source of bombarding particles nor the environment in which the deposition takes place. The principle criteria is that energetic particle bombardment is used to modify the film formation process and film properties. The effects of energetic particle bombardment on non-reactive and reactive film growth are discussed in Sects. 9.4.3 and 9.5.3.

The concept and application of ion plating was first reported in the technical literature in 1964[1][1a][2] with some justification of the terminology discussed in 1968.[3] The technique was initially used for improvement of the adhesion and surface coverage by PVD films. Later it was shown that the concurrent bombardment could be used to control film properties such as density and residual film stress. The technique was subsequently shown to enhance chemical reactions in the reactive deposition of compound thin films. An early review was written on the ion plating process in 1973[4] and the process has often been discussed in the literature since then.[5]–[8]

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There are two basic versions of the ion plating process. In "plasma-based ion plating," the negatively biased substrate is in contact with a plasma and bombarding positive ions are accelerated from the plasma and arrive at the surface with a spectrum of energies. In plasma-based ion plating, the substrate can be positioned in the plasma generation region or in a remote or downstream location outside the active plasma generation region. The substrate can be the cathode electrode in establishing a plasma in the system. In "vacuum-based ion plating," the film material is deposited in a vacuum and the bombardment is from an ion source ("gun"). The first reference to vacuum-based ion plating or vacuum ion plating was in 1973[9] and was used to deposit carbon films using a carbon ion beam.[10]

In a vacuum, the source of vaporization and the source of energetic ions for bombardment can be separate. This process is often called Ion Beam Assisted Deposition (IBAD).[11] Often the ion beam is "neutralized" by the addition of electrons so the beam is volumetrically neutral or a mixed ion/electron plasma is generated in the source. This prevents coulombic repulsion in the beam and prevents charge buildup on the bombarded surface. Figure 8-1(*a*) shows a simple plasma-based ion plating configuration using a resistively-heated vaporization source and Fig. 8-1(*b*) shows a simple vacuum-based (IBAD) system using an electron-beam evaporation source and an ion gun.

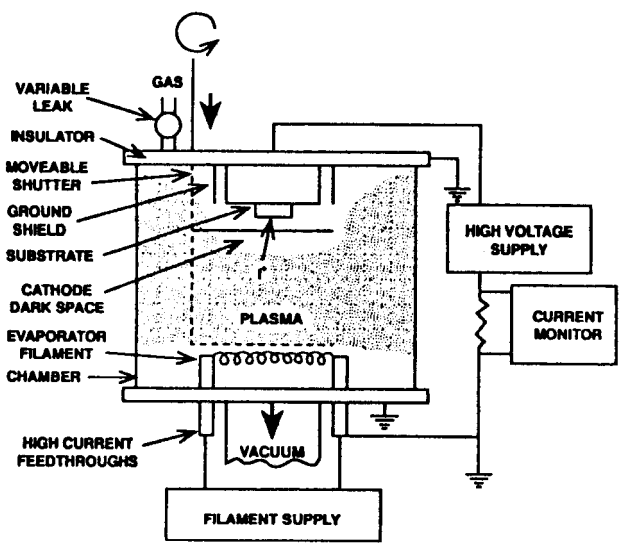


Figure 8-1(a). Plasma-based ion plating.

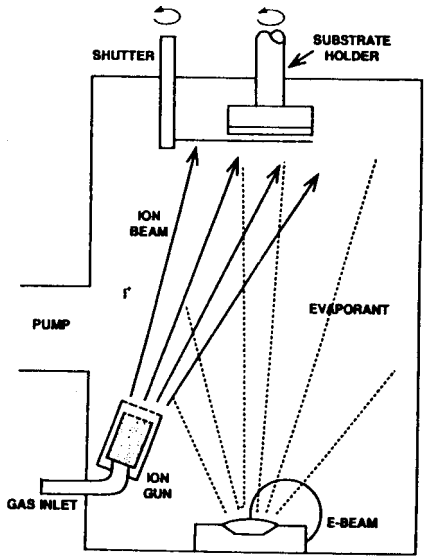


Figure 8-1(b). Vacuum-based ion plating.

In reactive ion plating, the plasma activates the reactive species or reactive ion species are produced in an ion source or plasma source. The bombardment enhances the chemical reactions as well as densifys the depositing film. The bombardment-enhanced interactions are complex and poorly understood.[12] In some cases, such as when using low-voltage high-current electron beam evaporation, arc vaporization, or postvaporization ionization, an appreciable portion of the vaporized film atoms are ionized to create film ions which can be used to bombard the substrate surface and growing film. Often the term ion plating is accompanied by modifying terms such as "sputter ion plating," "reactive ion plating," "chemical ion plating," "alternating ion plating," "arc ion plating," etc., which indicate the source of depositing material, the method used to bombard the film, or other particular conditions of the deposition.

The important parameters in non-reative ion plating are the mass and energy distribution of the bombarding species, and the flux ratio of bombarding species to depositing atoms. The flux ratio (ions/atoms) can be from 1:10 if energetic (> 500 eV) ions are used to greater than 10:1 if low energy (<10 eV) ions are used. Typically it is found that above a certain energy level, the flux ratio is more important in the modification of

film properties than is the bombardment energy. For example, for copper this specific energy is about 200 eV. Above that energy it is best to increase the flux ratio to modify the film properties. High energy bombardment can have differing effects from low energy bombardment. For example, low energy (~5 eV) bombardment promotes surface mobility of the adatoms and is used to aid in epitaxial growth,[13] while high energy bombardment generally promotes the formation of a fine-grained deposit. The energy distribution of the bombarding species is dependent on the gas pressure[14] so gas pressure control is an important process parameter in ion plating. In reactive ion plating, the chemical reactivity of the energetic bombarding and depositing species are important process parameters.

8.2 STAGES OF ION PLATING

The ion plating process can divided into several stages where the bombardment affects the film formation (Ch. 9):

1. The substrate surface can be sputter cleaned and the surface activated in the deposition chamber.
2. Bombardment during the nucleation stage of film deposition can increase the nucleation density and cause recoil implantation of depositing film atoms into the substrate surface.
3. Bombardment during interface formation adds thermal energy to the surface and introduces lattice defects into the surface region which promotes diffusion and reaction.
4. Bombardment during film growth densifys the film, causes recoil displacement of near-surface atoms (atomic peening), causes sputtering and redeposition and adds thermal energy. In reactive deposition, bombardment aids chemical reactions on the surface and the presence of a plasma activates reactive species. The bombardment can also preferentially remove unreacted species.

It is important that the surface preparation stage blend into the deposition stage so that there will be no recontamination of the substrate surface after *in situ* cleaning and activation. In some cases, the high potential and bombarding flux used for surface preparation must be

decreased during the nucleation stage in order to allow a film to form and not sputter away all of the depositing film atoms.

8.2.1 Surface Preparation (*In Situ*)

Surface preparation includes both cleaning and surface modification. Bombardment of the substrate surface by energetic particles prior to the deposition of the film material allows *in situ* cleaning of the surface (Sec. 12.10). Any surface placed in contact with a plasma will assume a negative potential (sheath potential) with respect to the plasma (self-bias) due to the more rapid loss of electrons to the surface from the plasma compared to the loss of ions to the surface. The sheath potential will accelerate ions across the sheath to bombard the surface. The voltage that develops across the sheath, depends on the flux and energy of the electrons striking the surface. For a weakly ionized DC plasma, the sheath potential will be several volts. Ions accelerated across this sheath potential can desorb adsorbed molecules such as water vapor ("ion scrubbing"). If the ions are of a reactive species, such as oxygen, they will react with contaminant layers, such as hydrocarbons, to produce volatile reaction products and clean the surface.

Higher negative sheath potentials can be developed on the substrate surface by accelerating electrons to the surface, applying a DC potential to an electrically conductive surface (applied bias), or by applying an rf or pulsed DC to an insulating surface. When the potential is high enough for the accelerated inert gas ions from the plasma to attain energies greater than about 100 eV, the ion bombardment can cause physical sputtering that cleans the surface by sputter cleaning. If a chemically reactive species, such as chlorine from CCl_4, is present, the surface may be cleaned by plasma etching if a volatile chemical compound is formed by the bombardment.[15]

Bombardment can also cause surface modification that can be conducive to film formation. For example, bombardment of a carbide surface by hydrogen ions results in the decarburization of a thin surface layer producing a metallic surface on the carbide,[16] and bombardment from a nitrogen plasma can be used to plasma nitride a steel surface prior to the deposition of a TiN film.[17][18]

Bombardment can also make the surface more "active" by the generation of reactive sites and defects.[19] For example, un-bombarded silicon surfaces metallized with aluminum shows no interdiffusion, but the

bombarded surface gives rapid diffusion.[20] If done at low bombarding energies, the cleaning of semiconductor materials can be done without introducing surface defects which affect the electronic properties of the surface/interface.[21]

8.2.2 Nucleation

In ion plating, it is important that bombardment of the substrate surface during the surface preparation stage be continued into the deposition stage, where film atoms (adatoms) are continually being added to the surface. Nucleation of adatoms on the surface is modified by concurrent energetic particle bombardment. This modification can be due to a number of factors including: cleaning of the surface, the formation of defects and reactive sites on the surface, recoil implantation of surface species and the introduction of heat into the near-surface region.[22] Generally, these effects increase the nucleation density which is conducive to good adhesion (Sec. 9.2). In addition, where there is high energy bombardment, sputtering and redeposition allows nucleation and deposition in areas which would not otherwise be reached by the depositing atoms.

8.2.3 Interface Formation

Bombardment enhances the formation of a diffusion or compound type interface on the "clean" surface if the materials are mutually soluble (Sec. 9.3). Bombardment enhances the formation of a "pseudodiffusion" type of interface due to the energetic particle bombardment, if the materials are insoluble. Interface formation is aided by radiation damage in the surface[19] and the deposition of energy (heat) directly into the surface without the necessity for bulk heating.[23][24] In some cases, the temperature of the bulk of the material can be kept very low while the surface region is heated by the bombardment. This allows the development of a very high temperature gradient in the surface region which limits diffusion into the surface.[25] Ion bombardment, along with a high surface temperature, can cause all of the depositing material to be diffused into the surface producing an alloy or compound coating.

8.2.4 Film Growth

Energetic particle bombardment during the non-reactive growth of the film can modify a number of film properties as discussed in Sec. 9.4.3. These include: density, bulk morphology, surface morphology, grain size, crystallographic orientation, electrical resistivity, and porosity. The changes in film properties are due to a number of factors including: heating of the surface region during deposition, recoil implantation ("atomic peening"), sputtering and redeposition, and sputtering of loosely bonded contaminant species.[26] The increase in film density is a major factor in modifying film properties such as hardness, electrical resistivity, index of refraction and corrosion resistance.

In cases where the bombarding energy is low (<5 eV), the mobility of the adatom on the surface can be increased by concurrent bombardment. This increased mobility assists in forming large grains and single crystal films (epitaxial growth).[13]

8.2.5 Reactive and Quasi-Reactive Deposition

In reactive deposition, an elemental material is vaporized and the depositing film material either reacts with the ambient environment or with a co-deposited material to form a compound. In reactive ion plating (or activated reactive ion plating), depositing species can react with the gaseous ambient or with a co-deposited species to form a non-volatile compound film material.[12][27]–[31] For example, depositing titanium atoms can react with "activated" gaseous nitrogen to form titanium nitride (TiN), or with co-deposited carbon to form titanium carbide (TiC), or with a combination of gaseous nitrogen and co-deposited carbon, to form titanium carbonitride (TiC_xN_y). In plasma-based ion plating, the plasma activates reactive species and/or can cause co-deposition of a reactive species from a chemical vapor precursor. The concurrent bombardment of the surface during reactive deposition enhances chemical reaction ("bombardment-enhanced chemical reactions") on the surface[12][15][32]–[34] desorbs un-reacted adsorbed species[26] and densifies the film.[35] In general, it has been found necessary to have concurrent bombardment in order to deposit hard and dense coatings of materials. Figure 6-11, shows the relative effects of heating and concurrent bombardment on the resistivity of ion plated and non-ion plated TiN films.[36] In vacuum-based ion

plating, where there is no plasma near the depositing film, bombardment of the depositing film by energetic reactive gas ions from an ion or plasma source, enhances the chemical reaction.[37][38]

In reactive deposition, the extent of the reaction depends on the plasma conditions, bombardment condition, and the availability of the reactive species. By limiting the availability of the reactive species, the composition of a deposit can be varied. For example, in the reactive ion plating of TiN, by reducing the availability of the nitrogen in the plasma at the beginning of the deposition, an initial layer of titanium is deposited. The composition can then be graded to TiN by increasing the availability of nitrogen in the plasma thus forming a "graded interfacial region."

In quasi-reactive ion plating a compound material is vaporized in a partial pressure of reactive gas that aids in replacing the species that are lost in the transport from the vaporization source to the substrate.[39]

Residual Film Stress

Concurrent or periodic bombardment of the growing film can introduce high compressive stresses. The residual stress can be controlled to give the desired stress level. This can be accomplished either by controlling the stress throughout the film or by depositing alternate layers of material with compressive and tensile stresses.[40][41]

Gas Incorporation

At low substrate temperatures, bombarding gas can be incorporated into the substrate surface during sputter cleaning and into the growing film, particularly if the bombarding energy is high.[42][43] Gas incorporation can lead to void formation in the film or the loss of adhesion of a film deposited on a substrate surface containing incorporated gas from sputter cleaning.[44] Gas incorporation can be minimized by having a high substrate temperature (> 300°C) where the gas will be continually desorbed. To minimize gas incorporation at low deposition temperatures, the bombarding energy should be kept low (i.e., less than 300 eV), or a heavy bombarding particle (e.g., krypton or mercury) can be used. Low-temperature bombardment can be used to deliberately incorporate large amounts of gas in deposited films.[45][46]

Surface Coverage and Throwing Power

Surface coverage is the ability to cover a large and/or complex surface such as, for example, to coat the back-side of a sphere which faces away from the vapor source. This front-to-back thickness ratio is a measure of the surface covering ability of the deposition process. In plasma-based ion plating much of this ability derives from scattering in the gaseous deposition environment[47] The higher the gas pressure, the smaller the front-to-back thickness ratio. Gas scattering alone tends to give vapor phase nucleation of ultrafine particles and a low density deposit.[48] The ion bombardment densifies the deposited material so that relatively high gas pressures can be used and still attain a dense deposit.

Throwing power is a measure of the ability of the depositing material to coat into microscopic surface features such as porosity and vias, and over surface features such as bumps such as seen in Fig. 5-8. The sputtering/redeposition of the depositing film material during ion plating gives a high throwing power on the microscopic level.[49]–[53] This throwing power results in better "filling" of surface features such as vias and in fewer pinholes in ion plated films on rough surfaces than with either sputter deposition or vacuum evaporation.[54] When depositing an alloy, preferential sputtering of materials at a high angle-of-incidence, such as on the side of a bump, during deposition can give very localized compositional variations.[55]

Ion plating, using "film ions," is used to fill vias and trenches on semiconductor surfaces by sputter deposition. By postvaporization ionization of the film atoms and accelerating the ions to the surface they arrive with a more near normal angle-of-incidence (collumination) than if they were sputter deposited without ionization and acceleration.[56][57]

Film Properties

Films deposited by ion plating can have very high residual compressive stresses due to atomic peening by the concurrent energetic particle bombardment. These compressive stresses can lead to spontaneous failure of adhesion. The films can also contain a high concentration of "trapped" gas which can be released on heating. The bombardment can produce a very fine-grained or even amorphous material. The preferred crystallographic orientation of the grain structure can be modified by the extent of the bombardment. When deposited under optimum conditions, films

deposited by ion plating can have a density approaching that of the bulk material, low residual stress and no gas incorporation.

8.3 SOURCES OF DEPOSITING AND REACTING SPECIES

The film material being deposited in the ion plating process can come from any source of condensable material including thermal vaporization, sputtering, arc vaporization and chemical vapor precursors. Thermal vaporization is generally used when high deposition rates are desired, while sputter deposition is used when a lower deposition rate is acceptable. Thermal vaporization and sputter deposition can be combined in the same system. For example, sputter deposition can be used to co-deposit the minor constituent of an alloy while thermal vaporization is used to co-deposit the major constituent.

8.3.1 Thermal Vaporization

Thermal vaporization has the advantages that it is low cost, energy efficient and the vaporization rates can be very high (Ch. 5). Various thermal vaporization sources can be used in ion plating. For plasma-based ion plating, the resistively heated sources are often used. Low energy electron beam heating from hollow cathode discharge (HCD)[58]–[62] sources and electron sources can be used, often with a magnetic confining field. This allows the electrons both to heat the material to be vaporized and also to create the plasma. High-energy hot-filament electron beam heating can be used with a plasma but this requires isolating the electron emitting filament from the plasma by the use of a conductance baffle with a hole to allow the electron beam to enter the plasma/crucible region (differentially pumped e-beam).[63]–[65] Even in a good vacuum, e-beam evaporation ionizes some of the evaporated material and a bias can be used to accelerate these ions to the depositing film. Alloy materials can be deposited by thermal vaporization.[66] The thermal vaporization in the Jet Vapor Deposition process has been combined with ion bombardment to modify the properties of the deposited coating.[67] Postvaporization ionization of the thermally vaporized atoms and gas atoms/molecules in the gaseous environment can be enhanced by using an auxiliary plasma (Sec. 8.4.1).

8.3.2 Physical Sputtering

Physical sputtering (Ch. 6) is often used for vaporizing the material to be deposited. However when using DC magnetron sputtering configurations, the plasma is confined in a region near the target and is not available as a supply of ions for substrate bombardment nor for activation of reactive species. Plasma generation in the space between the target and the substrate can be attained using an auxiliary plasma (Sec. 8.4.1) or unbalanced magnetron sputtering. The auxiliary plasma also aids in the postvaporization ionization of the sputtered material.

8.3.3 Arc Vaporization

Low-voltage high-current arc vaporization (Ch. 7) can be used as a source of the depositing material, and to provide ions for bombardment as well as for activating reactive gases for reactive ion plating. The vaporized material can come from a solid water-cooled cathode (cold cathodic arc) or from a molten anode (anodic arc). If the arc is established with a gas present, giving a "gaseous arc," both the vaporized material and gaseous species are ionized.[68]

The cathodic arc source and a sputtering source can be combined into one design.[69]–[70] It has been found that by using the arc discharge to supply the ions for sputter cleaning the substrates, the cleaning and heating can be performed much faster than when using a DC diode discharge, due to the high ionization and the multiply-charged heavy metal ions in the arc discharge. The use of arc vaporization to deposit the initial layer of film allows the formation of a very adherant film. By building the film thickness by sputter deposition, the deposition of "macros" is avoided.

Gaseous arc vaporization in a reactive gas has the advantage that the arc is a very good source for "activating" the reactive gas and thus increase its chemical reactivity. The cathodic arc moves over the whole target surface and thus prevents poisoning of some areas of the target surface which can be a problem in reactive magnetron sputter deposition. Cathodic arc vaporization sources are widely used in the tool coating industry to deposit nitride, carbides and carbonitrides using a bias on the substrate.[69]–[71]

8.3.4 Chemical Vapor Precursor Species

Gaseous chemical vapor precursor species containing the material to be deposited can be used as a deposition source in ion plating. Using a chemical vapor precursor species in the plasma is similar to Plasma Enhanced Chemical Vapor Deposition (PECVD) where the plasma is used to decompose the chemical species and bias PECVD where ions from the plasma of precursor vapors are accelerated to the substrate surface at low pressures.[72] Typical chemical vapor precursors are, $TiCl_4$ for titanium,[28] SiH_4 for silicon and CH_4 (methane), C_2H_2 (acetelyene) and C_2H_6 (ethane)[73] for carbon, diamond-like carbon (DLC) and diamond film deposition. The chemical vapor precursor may not be completely dissociated and can deposit a film containing impurities such as hydrogen from the hydrocarbons or chlorine from the chlorides. The chemical vapor precursor can be injected into the plasma in plasma-based ion plating[73]–[75] or into a confined plasma ion source in vacuum-based ion plating.[72][76][77] In the plasma, some of the precursor material is fragmented and a portion of the fragments is ionized. These film-ions can then be accelerated to bombard the growing film.

Precursor vapor can be formed by sputtering an elemental target with a plasma containing an etch gas (e.g., Cl_2, CCl_4, CCl_3, F, $CClF_3$ for silicon). The precursor vapor can then be decomposed to give a film on the substrate. This method of sputtering is reported to give a film deposition rate of 5–30 times that of reactive sputter deposition using no etch gas.[78]

8.3.5 Laser-Induced Vaporization

Laser radiation can be used to vaporize the surface of a material.[79] Laser vaporization creates a large number of ions in the vapor "plume" and these can be accelerated to the substrate surface. This technique has been used to deposit hydrogen-free diamond-like carbon (DLC) films.[80] Laser vaporization with concurrent ion bombardment has been used to deposit high quality high-temperature superconductor films at relatively low substrate temperatures.[81]

8.3.6 Gaseous Species

Gaseous species, such as oxygen and nitrogen can provide one reacting species in reactive ion plating. Since the mass of these species is low compared to most of the condensable depositing species, ions of these species are not as effective in modifying the film properties as are heavier ions such as those of argon. For this reason, in reactive ion plating, a mixture of reactive and inert gaseous species is often used just as it is in reactive sputter deposition where argon is more effective in sputtering than is oxygen or nitrogen ions.

8.3.7 Film Ions (Self-Ions)

The use of high energy ions of the condensable film materials (film or self ions) is a special case where the depositing and bombarding species are the same. The advantage is that since the masses of the target and bombarding species are the same, maximum momentum and energy is transferred during collision and there is no problem with gas incorporation in the deposited film.[82] Film ions are obtained during arc vaporization, laser vaporization, and by postvaporization ionization in sputtering and thermal evaporation. Often film ions are mixed with neutral film species and the composition of the flux is not known. In some cases, the film ions are deflected so that a pure film ion beam is deposited such as in the use of a plasma duct to eliminate globules from an arc source (Sec. 7.3.1).

8.4 SOURCES OF ENERGETIC BOMBARDING SPECIES

The energetic species used to bombard the growing film can be either ions or neutrals although acceleration of charged ions is the most common way to obtain a controlled bombardment. Ion plating is like sputtering, except that the sputtering target is now the growing film and often the surface is a complex shape. The bombardment ratio (energetic particles to depositing atoms), the particle energy, and energy distribution are important parameters in the ion plating process. The energy should be high enough to give appreciable energy transfer on collision but should not

be high enough to physically implant the bombarding gases in the depositing film where it can precipitate and form voids.

The ratio of bombarding species to depositing atoms (flux ratio) is important to the film properties.[83][84] Typically, to complete the disruption of the columnar morphology of the growing film to give the maximum density and least microporosity, the energy deposited by the bombarding species should be about 20 eV per depositing atom or give about 20–40 % resputtering.[85][86] Early studies equated resputtering to film quality.[87]

In plasma-based ion plating, the ion flux and flux energy distribution are difficult to measure directly. When using low-pressure sputtering as the vapor source, the presence of high energy reflected neutrals from the sputtering target can be an important parameter which is often not recognized nor controlled. In both vacuum-based and plasma-based ion plating, bombardment and deposition consistency and reproducibility is usually controlled by having a consistent vaporization source, system geometry, fixture motion, gas composition, gas flow, and substrate power (voltage and current).

8.4.1 Bombardment from Gaseous Plasmas

Plasma-based ion plating is the most common ion plating configuration. The most common inert gas species used for plasma formation and ion bombardment is argon, because it is the least expensive of the heavy inert gases. Krypton and xenon are sometimes used to establish the plasma. Common reactive gases used in the plasma are nitrogen, methane, and oxygen. Often a mixture of inert gas and reactive gas is used to increase the momentum transfer efficiency in reactive deposition.

The plasma can be formed using a number of configurations as described in Ch. 6. The most common configuration is the DC diode where an electrically conductive substrate is the cathode. When the substrate or the depositing film is an electrical insulator, the plasma can be formed by making the substrate an rf electrode in an rf plasma system[88][89] or a pulsed DC can be used. In some cases, the plasma can be enhanced by an auxiliary electron source or by the electrons used to evaporate the source material.

Auxiliary Plasmas

In some PVD configurations, such as magnetron sputtering, the plasma is confined to a position away from the substrate. This decreases the amount and uniformity of the substrate bombardment that can be attained. In order to attain a higher flux and more uniform bombardment, a totally separate plasma (auxiliary plasma) can be established. These auxiliary plasmas can also be used to enhance ionization of the vaporized film species (i.e., postvaporization ionization). Auxiliary plasmas can be formed using a hot electron-emitting filament,[90] a hollow cathode,[59][60][91]–[93] a plasma arc source,[94] an unbalanced magnetron, or a dual magnetron source.[95] The electrons can be confined with a magnetic field which increases the electron path length.

8.4.2 Bombardment from Gaseous Arcs

Low-voltage high-current arcs are a source of ions. The most common ion plating configuration uses a gaseous plasma where ions of both the gas and the vaporized materials are used to bombard the growing film.[68][96] The ions from the arc can be used to sputter clean the surface at a high current density. If the accelerating voltage is high enough, the ion bombardment can prevent any net deposition on the substrate.[59][97]

8.4.3 Bombardment by High Energy Neutrals

In sputter deposition, ions bombarding the sputtering cathode can be neutralized and reflected with an appreciable portion of their incident energy. If the gas pressure is low (<≈3 mTorr), the high energy reflected neutrals will not be thermalized by collisions and can bombard the growing film and affect the film properties.[98]–[100] The flux of reflected energetic neutrals may be anisotropic giving anisotropic properties in the resulting deposited film. For example, the residual film stress in post-cathode magnetron sputtered deposited films depends on the relative orientation in the film with respect to the post orientation.[40][41][101] A major problem with energetic neutral bombardment is that it is often unrecognized and uncontrolled, particularly if there is poor pressure control of the sputtering system. High energy neutrals are also formed by charge exchange processes in the higher-pressure DC diode plasma configurations where the substrate is the cathode.[102]–[104]

8.4.4 Gaseous Ion and Plasma Sources (Guns)

Ion sources, such as are used in the IBAD process, were discussed in Sec. 4.5. The most common ion sources are the Kaufman ion source used for inert gas ions[105] and the End-Hall ion sources used for reactive gas ions.[106] Where very high ion currents are needed the inductively coupled ion source is sometimes used.[107] The ion source can either produce a monoenergetic ion beam (e.g., Kaufman ion source) or produce a beam with a spectrum of ion energies (e.g., Hall source). In many instances, the beam from an pure ion source such as the Kaufman source is "neutralized" by the addition of electrons so that the beam will not diverge due to coulombic repulsion and any surface charge buildup will be neutralized. Helicon plasma[107][108] or ECR[107]–[109] discharge plasma sources can also be used. When using high energy ions to give concurrent bombardment during deposition, care must be take that gas incorporation does not produce undesirable film properties.

8.4.5 Film Ion Sources

Ions of the film material can be used for deposition. Energetic ions of the depositing film material are effective in modifying film properties since their mass matches the mass of the "target atom" in the film surface and thus the momentum transfer during collision is maximized and gas entrapment is not a problem as it can be in using argon ion bombardment. Many ion sources have been developed to produce a metal ion beam.* Many of these sources were developed for isotope separation projects.[110] Vacuum arc sources for producing a pure metal ion beam are available commercially.[111] Low pressure gaseous arc sources for producing a mixed metal ion and gas ion beam are also available. A pure metal ion beam can be formed by field ionization and such sources are available commercially. When using a beam of film ions, the energy of the

*In the early days of reporting the effects of the ion plating process, the author received a call from a person complaining that they could not reproduce the effects reported and could not even get a film to form. After some discussion, it became clear that the person was using a pure film-ion beam at 30,000 eV energy from a calutron isotope separator source. Obviously, the sputtering rate was higher than the deposition rate.

depositing species must be kept low or self-sputtering will completely sputter the deposited material. A disadvantage of using film ions is the difficulty of obtaining a high flux source.

Postvaporization Ionization

The degree of ionization of a vapor sputtered or evaporated into a plasma is minimal. In particular in magnetron sputtering, few of the sputtered atoms are ionized in the plasma, due to the low density plasma and the short path length through the plasma. The ionization of species vaporized by evaporation or sputtering can be enhanced by postvaporization ionization either by passing the vapor through a high-density low-energy (100 eV) electron cloud or through a high electron-density auxiliary plasma. Such plasmas can be formed by a hot filament discharge,[112] hollow cathode discharge, rf discharge,[47][48][113]–[117] unbalanced magnetrons, dual unbalanced magnetrons,[95] or inductively coupled plasma discharge.[107] Using rf ionization, ion fractions of as high as 70% have been reported.[56] The ions thus formed can then be accelerated under a substrate bias and impinge on the substrate at a near-normal angle-of-incidence. This technique can be used to enhance the filling of vias in semiconductor device fabrication and is one type of "collimated deposition."[56][57]

Figure 8-2 shows several configurations that can be used for postvaporization ionization. Figure 8-2(*a*) shows the evaporation of material using a low-voltage, high-current hot hollow cathode source with magnetic field confinement. The material that is vaporized passes through the electron beam and an appreciable portion of the metal vapor is ionized. These film ions can be accelerated and used to clean the substrates at high energies and then deposit a film by lowering the accelerating voltage. This configuration has been used to deposit adherent silver films on beryllium substrates for diffusion bonding.[58][59] Figure 8-2(*b*) shows post vaporization ionization using an rf coil above the thermal vaporization source.[116] Figure 8-2(*c*) shows the use of an electron emitting filament to enhance ionization and Figure 8-2(*d*) shows the use of opposing dual unbalanced magnetron for ionization. Figure 8-2(*e*) shows the use of a magnetic field above a cathodic arc source to enhance ionization and aid in vaporizing "macros." Figure 8-2(*f*) uses a hot hollow cathode for an electorn source.

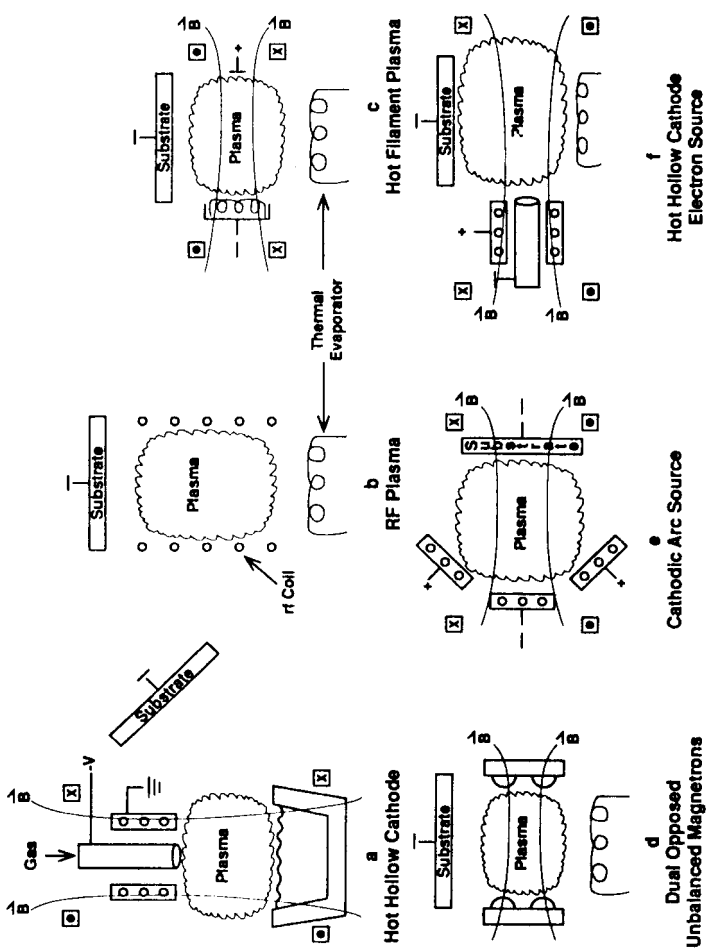


Figure 8-2. Auxiliary plasmas for postvaporization ionization.

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8.4.6 High Voltage Pulsed Ion Bombardment

The technique of Plasma Immersion Ion Implantation (PIII) (Sec. 2.5.2) can be combined with a film deposition process such as sputtering or plasma enhanced CVD to give an ion plating process that is called Plasma Immersion Ion Processing.[118]

8.5 SOURCES OF ACCELERATING POTENTIAL

Ions are accelerated in an electric field gradient and are accelerated normal to the equipotential surfaces. A problem with applying a voltage to the substrate is that the substrate (or fixture) is often an irregular shape and this causes the equipotential surfaces around the fixture to have irregular shapes. In IBAD processing the acceleration voltage in an ion gun extraction grid accelerates the ions away from the source to a substrate that is at ground potential. In plasma-based ion plating, the accelerating potential is on the substrate or on a high-transmission grid just in front of the substrate.

8.5.1 Applied Bias Potential

A simple negative DC bias potential can be applied directly to an electrically conducting surface which can be the cathode of a DC diode discharge. Bombardment will be relatively uniform over flat surfaces where the equipotential field lines are conformal to the surface, but will vary greatly if the field lines are curved since ions are accelerated normal to the field lines. The DC diode discharge that is generated will fill the deposition chamber volume if the pressure is sufficiently high, although the plasma density will vary with position in the chamber.

In the application of a DC potential, often the applied voltage and current (power—watts/cm^2) to the surface are used as process parameters and control variables. However it must be realized that the bombarding ions generally have not been accelerated to the full applied potential due to the position of their formation, charge exchange collisions, and physical collisions in the gas. The measured current consists of the incident ion flux (the ions may be multiply charged) and the loss of secondary electrons from the surface. The cathode power is a useful process parameter to

maintain reproducibility only if parameters such as gas composition, gas pressure, system geometry, etc., are kept constant.

The bias can be in the form of a low frequency AC potential[119] but the pulsed DC bias is becoming more common. The pulsed DC bias (Sec. 4.4.3) uses a bipolar square waveform operating at 10–100 kHz and is an AC-type of configuration where the on-off time and pulse polarity can be varied.[120]–[123] During the off-time, plasma species can move to the substrate surface and neutralize any charge build-up. The current-voltage behavior of the discharge changes during the pulse. Initially the impedance is high, giving a high voltage and low current. As the discharge develops, the impedance is lowered, the voltage decreases, and the current increases. The behavior of the impedance depends on the composition of the gas. For example, the impedance change will be greater for an oxygen discharge than for an argon discharge. The pulsed DC bias technique can be used to allow bombardment of electrically insulating films and surfaces without arcing and allow more unifom bombardment of irregular surfaces.

A radio-frequency (rf) bias potential (Sec. 4.4.6) can be applied to the surface of the substrate or depositing film when the surface or film is an electrical insulator to allow high energy ion bombardment.[124] The rf also prevents charge buildup on the surface which will result in arcing over the surface or through the insulating film if it is thin.[125] When applying an rf potential, the potential of the surface in contact with the plasma will be continuously varying, though it will always be negative with respect to the plasma. The DC bias of the surface with respect to the plasma will depend on the rf frequency,[126] the electrode areas, the presence of blocking capacitance in the circuit and whether an external DC bias supply is present. The energy of the ions that bombard the surface will depend on the frequency of the rf and the gas pressure. Maximum bombardment energy will be attained at low frequencies and low gas pressures. When using rf sputtering as a vapor source, a different rf frequency and power can be used on the substrate than is used on the sputtering target.[120]

The rf bias has the advantage that it can establish a discharge in the space between the electrodes at a pressure lower than that required for a DC bias. It has the disadvantage that the rf electrode is like a radio antenna and the plasma density formed over the surface depends on the shape of the substrate/fixture system. In all cases, ground shields should be kept well away from the rf electrode since the rf power can then be coupled directly to ground and not the plasma. In the case of an insulating substrate, the substrate must completely cover the rf electrode or the exposed metal will

provide a low resistivity (short) between the metal electrode and the plasma. When using an rf bias, the rf can be coupled into the fixture without electrical contact.[127] This is an advantage when using moving fixturing and tooling.

A combined DC bias and rf bias can be applied if an rf choke is used in the DC circuit to prevent the rf from entering the DC power supply. By applying a DC bias along with the rf bias, the insulating surface is exposed to bombardment for a longer period of time during the rf cycle.

8.5.2 Self-Bias Potential

A negative self-bias is induced on an insulating or floating surface in contact with a plasma, due to the higher mobility of the electrons compared to the ions. The higher the electron energy and flux, the higher the negative self-bias that is generated. Figure 8-3 shows a means of inducing a high self-bias by accelerating electrons away from an electron-emitting source and magnetically confining them so that they must bombard the substrate surface.[128] It is possible to generate a positive self-bias if the electrons are prevented from bombarding the surface by using a magnetic field, since positive ions can reach the surface by scattering and diffusion while the electrons are easily deflected away from the surface. For example, substrates in a post cathode magnetron sputtering system can have a positive self-bias since the electrons are kept from bombarding the substrate surface by the magnetic field parallel to the post sputtering target.

8.6 SOME PLASMA-BASED ION PLATING CONFIGURATIONS

Plasma-based ion plating is the most common ion plating technique. In plasma-based ion plating, the plasma can be generated with the substrate or substrate fixture as the active electrode in plasma generation or as an auxiliary cathode in a triode configuration.[129] Figure 8-4 shows some possible substrate-plasma configurations. A major concern is to obtain a uniform bombardment over the substrate surface during deposition. If the bombardment is not uniform then the film properties will not be uniform over the surface.

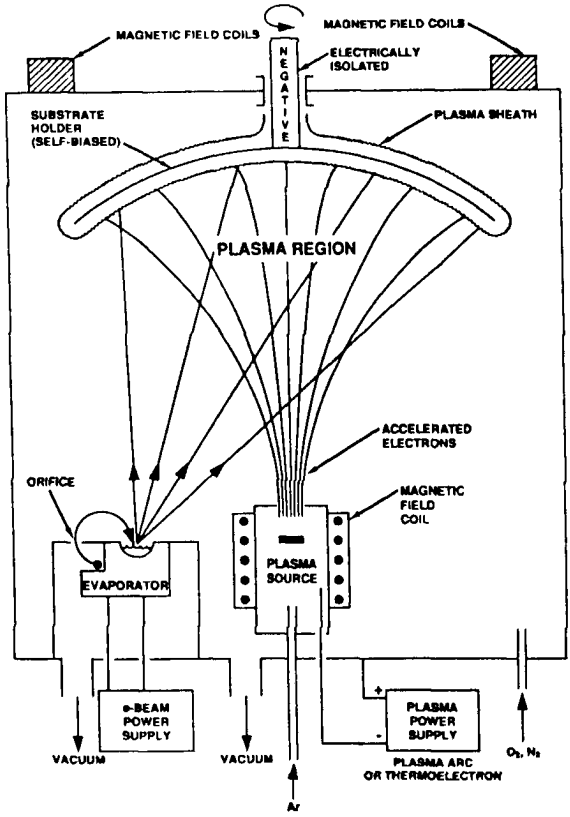


Figure 8-3. Applying a self-bias to an insulating or electrically floating surface (adapted from Ref. 128).

8.6.1 Plasma and Bombardment Uniformity

In plasma-based ion plating, ions are extracted from a plasma and accelerated to the substrate surface under an applied or self-bias potential. The flux and energy of ions from the plasma will depend on the plasma density and the electric field configuration. Plasma density and plasma properties were discussed in Sec. 4.2.2.

When a potential is applied to a flat surface, the electrical equipotential surfaces are conformal to the surface. When the surface is not flat the equipotential surfaces are curved in some regions and may not be able to follow re-entrant surface morphologies. When ions are accelerated to

the substrate surface, they will be accelerated in a direction normal to the equipotential surfaces. This means that the angle-of-incidence of the bombarding particles will be normal to the surface where the equipotential surfaces are conformal to the surface. When the equipotential surfaces are curved the ions will be focused or defocused on the surface. If the equipotential surfaces do not penetrate the re-entrant regions some areas may not be bombarded. Figure 4-2 shows some of the possible configurations. Obtaining uniform bombardment over a complex surface is often difficult.

8.6.2 Fixtures

Fixturing is an important aspect in obtaining bombardment uniformity and in obtaining the product throughput desired. A number of fixture configurations are shown in Fig. 3-12. If the surface to be coated is flat, then the fixture can be as simple as a pallet. When there is a large number of pieces, the fixturing should allow the plasma to form over all the surfaces. For example, in coating drill bits, the pieces can be mounted in a solid plate like a forest of posts and the plate rotated to randomize the deposition direction. The separation between drills is usually taken to be twice the diameter of the drill bit. The problem is that when a continuous DC plasma is formed, the plasma density near the plate will be less than near the tip and so the bombardment will be less at the base. This means that the surface will not be cleaned as well in this region. Also, the drills on the perimeter will be bombarded differently than those in the center. Another approach is to have a fixture which allows each drill to be rotated into a position where it will periodically get the maximum bombardment but will be subjected to some bombardment all the time as shown in Fig. 3-13. This type of fixture is much more expensive that the plate fixture.

Where the surfaces are very complex or moving, a high transmission grid can be used to give a more uniform bombardment. When coating small parts, the parts can be held in a grid or cage structure as shown in Fig. 8-5.[130]–[135] The parts can be tumbled to allow coating on all areas and is analogous to barrel-plating in electroplating.

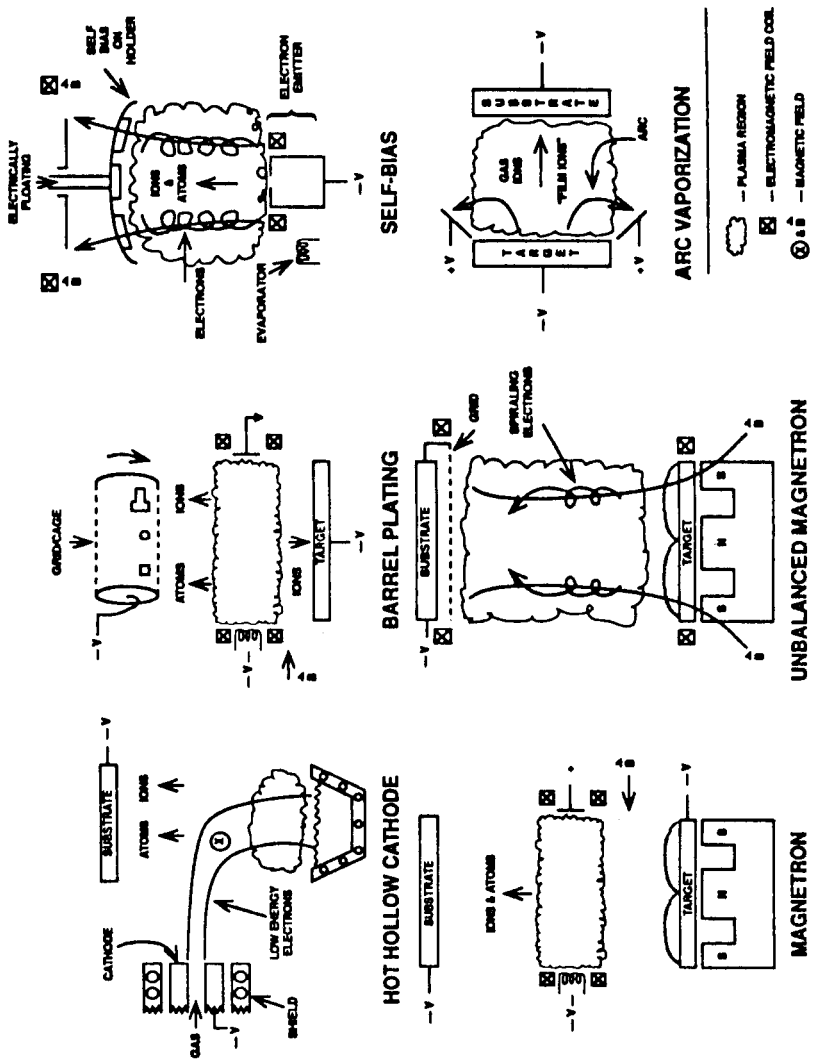


Figure 8-4. Substrate-plasma configurations.

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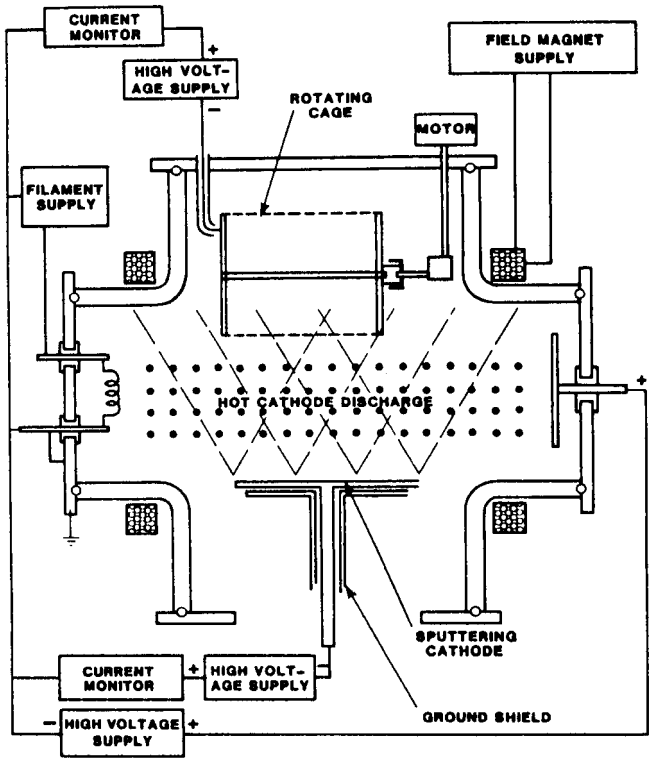


Figure 8-5. Sputter cleaning and ion plating small parts in a "barrel-plater."[130]

8.7 ION BEAM ASSISTED DEPOSITION (IBAD)

Ion Beam Assisted Deposition (IBAD) utilizes a separate vaporization source and bombardment source and is often classed as a deposition technique separate from ion plating. Figure 8-1(*b*) shows one IBAD configuration and Fig. 8-6 another configuration. Generally, bombardment is by gaseous ions from an ion or plasma gun. One advantage of the IBAD process is that in the IBAD process the ion flux can be measured directly by using a Faraday cup ion collector and atom flux can be measured using a mass deposition monitor such as a quartz crystal deposition monitor. A disadvantage is that plasma-activation processes are not operational for reactive deposition and the equipment costs are much higher than the plasma-based ion plating processes. IBAD can also be done

in a periodic fashion (alternating ion plating) where several monolayers of the condensable film material is deposited followed by bombardment by an inert[136] or reactive[137] species. This can easily be done using a drum fixture as shown in Fig. 3-12b.

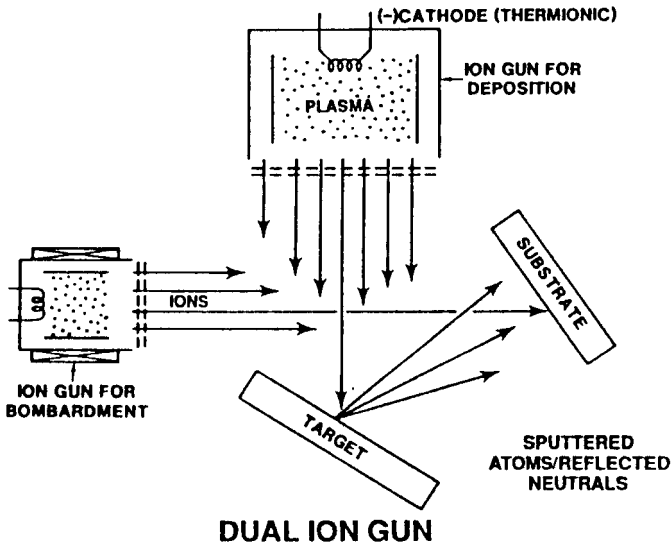


Figure 8-6. IBAD configurations using two ion guns.

Figure 8-7 shows a configuration using an ion/plasma source for the condensible species from a chemical vapor precursor and also for the ions used to bombard the depositing film. The ions can be from a carrier gas as well as from the chemical vapor precursor species.[72][77]

8.8 PROCESS MONITORING AND CONTROL

In most cases, the ion plating process relies on reproducible conditions and geometries to give reproducible film properties. For the most simple case where the substrates/fixtures are the cathode of a DC diode discharge, the process variables that should be reproduced include:

system and electrode geometry, substrate temperature, gas composition and pressure (or partial pressures), substrate potential, vaporization (deposition) rate of the depositing material, and mass flow rates if a reactive gas is used.

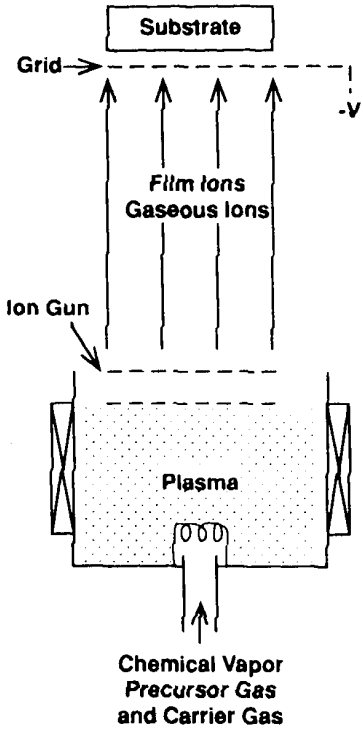


Figure 8-7. IBAD using a chemical vapor precursor species and an acceleration grid in front of the substrate.

8.8.1 Substrate Temperature

For the highest density deposit and the most complete reaction in reactive ion plating, an elevated temperature is generally desirable.[138] For example, in coating steel machine tools the tool is often heated to just below the tempering temperature (~450°C). The substrates are often held in moving fixtures, so generally the best technique for heating them is either by radiant heating or by electron or ion bombardment. Heating by

ion bombardment may result in too much sputtering and/or gas incorporation so it may be better to heat by radiant heating, then use ion bombardment to sputter clean and maintain the substrate temperature. The substrate temperature can be monitored using an infrared pyrometer that is programmed to read the maximum temperature that it sees.

In some cases, ion plated films are deposited with minimal heating of the substrate This is particularly advantageous when the substrate is thermally sensitive such as many plastics. For thermally sensitive substrates, the deposition can be periodic to allow cooling of the substrate between depositions. For example, the substrates can be mounted on a drum and periodically rotated in front of a deposition source and allowed to cool between depositions.[136][137]

8.8.2 Gas Composition and Mass Flow

Gas composition is an important processing variable in ion plating. The gas used for an inert plasma should be free of contaminants such as water vapor and oxygen that will become activated in the plasma. Inert gases can be purified using heated reactive surfaces such as copper, titanium, or uranium chip beds. Reactive plasmas should be free of contaminants. In reactive gases or gas mixtures, water vapor can be removed by cold traps utilizing zeolite adsorbers.

The amount of gas flowing into a system can be measured by mass flow meters and controlled by mass flow controllers as discussed in Sec. 3.5.8. In many instances, several gases are used at the same time. These gases can be premixed but often they are mixed in the gas manifolding systems and the partial flow of each gas is measured separately. In reactive deposition, the reactive gas availability and plasma activation can be important variables that are sensitive to the fixture/system geometry. If this is the case, then the injection of gas into the system is an important design consideration.[139] Often gas manifolding with multiple inlets is used to obtain uniform gas distribution in the deposition system.

8.8.3 Plasma Parameters

The first step in obtaining a reproducible plasma is to control the partial pressures of gases in the system, the total pressure and the mass flow of gases into the system. This requires that the vacuum gauges and

flow meters be calibrated and that gas purity be maintained. Contaminant release during processing may present control problems.

Plasmas are established and maintained by injection of power into the gas by means of an electric field. The uniformity of the field and the field gradients are important to obtaining a plasma with desired plasma properties. Plasma properties can be measured using techniques discussed in Sec. 4.2.2 though obtaining good spatial resolution is a problem. Generally, in an ion plating system, the plasma properties will vary with position in the system and it is important to measure the plasma properties at the same position each time. Differentially-pumped mass spectrometry[140] and optical emission spectroscopy[141][142] are often used to monitor and control the density of species in the plasma. Optical emission spectroscopy has the advantage that the output is more related to the plasma properties as well as the density of species.

8.8.4 Deposition Rate

In ion plating where some or much of the depositing material is being sputtered, deposition rate monitoring has some uncertainties. A reproducible deposition rate is often attained by using reproducible vaporization and bombardment conditions and the deposition rate is not measured directly. When using a thermal or arc vaporization source, where the spacing between source and substrate are large, quartz crystal monitors or optical adsorption monitors can be used. When using a sputtering vaporization source, optical adsorption monitors can be used.

8.9 CONTAMINATION IN THE ION PLATING PROCESS

In ion plating, contaminants can come from the evaporation source or the sputtering source. In addition, there are other sources of contaminants in an ion plating system.

8.9.1 Plasma Desorption and Activation

Plasmas in contact with surfaces will "ion scrub" the surface giving desorption of adsorbed surface species such as water vapor. The plasma will "activate" any reactive or potentially reactive species. The reduced pumping speed that is usually used in establishing a plasma, limits the rate of removal of contaminate species from the processing chamber. Water vapor in the processing chamber is often a major processing variable. Desorbed water vapor can be pumped in the processing chamber using properly shielded cryopanels.

8.9.2 Vapor Phase Nucleation

Vapor phase nucleation can occur in a dense vapor cloud by multibody collisions and nucleation to produce ultrafine particles. These particles have a size range of 10–1000 Å and the size and size distribution of the particles is dependent on the gas density, gas species, evaporation rate and the geometry of the system. Formation of the ultrafine particles in a plasma results in the ultrafine particles having a negative charge. Since the particles have a negative charge, they will not deposit on the negatively-biased substrates. The particles will tend to be suspended in the plasma near the walls and will deposit on the chamber walls and the substrates when the plasma is extinguished and the bias is removed.* In ion plating, the higher the vaporization rate and the higher the gas pressure the more ultrafine particles will be formed.

The particulates should be swept through the vacuum pumping system as much as possible. This is best done by keeping the plasma on and opening the conductance valve to extinguish the plasma by reducing the pressure rapidly. The bias potential on the substrates should be retained until the plasma is extinguished.

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*In the early work on ion plating, the particles formed in the plasma and deposited on the walls were called "black sooty crap" (BSC) and could be very pyrophoric. One game was to ask an observer to wipe the particles off a window with a paper towel. When the window was wiped, the towel caught on fire and a flame front moved over the surface of the chamber.

8.9.3 Flaking

Flaking of deposited films in an ion plating system is due to thickness buildup, residual film stress, and surface roughness (pinhole flaking). It is exacerbated by the contamination of surfaces by ultrafine particles which prevent adhesion of the deposited film to surfaces in sequential deposition runs. This means that an ion plating system probably should be cleaned more often than a sputter deposition or vacuum deposition system.

8.9.4 Arcing

The presence of a plasma means that there can be charge buildup on insulating surfaces in the system and this can vary with position in the plasma. This charge buildup on surfaces can cause arcing that produces particulates in the deposition system. The high throwing power of the ion plating process can allow film deposition on high voltage insulators, such as those used on high voltage feedthroughs. This film can then cause arcing over the insulator surfaces. High voltage insulators in an ion plating system should be well shielded from film deposition. The shields must be closely spaced to prevent a glow discharge from being formed between the shields.

8.9.5 Gas and Vapor Adsorption and Absorption

The deposition of particulates and poorly adherent films on the vacuum surfaces will cause rapid deterioration of the pump-down time due to gas and vapor adsorption on the high surface areas. The absorption of some gases, such as hydrogen, into the vacuum materials from a plasma is higher than from a gaseous environment. For example, when using a hydrogen plasma, the hydrogen adsorption rate in stainless steel will be about 1000 times the adsorption rate from gaseous hydrogen.

8.10 ADVANTAGES AND DISADVANTAGES OF ION PLATING

Some possible advantages to ion plating are:[4][5][143]

- Excellent surface covering ability ("throwing power") under the proper conditions.
- Ability to have *in-situ* cleaning of the substrate surface.
- Ability to introduce heat and defects into the first few monolayers of the surface to enhance nucleation, reaction, and diffusion.
- Ability to obtain good adhesion in many otherwise difficult systems.
- Flexibility in tailoring film properties by controlling bombardment conditions—morphology, density, residual stress.
- Equipment requirements are equivalent to those of sputter deposition.
- Source of depositing material can be from thermal vaporization, sputtering, arc vaporization, or chemical vapor precursor gases.
- Enhancement of reactive deposition process—activation of reactive gases, bombardment-enhanced chemical reaction, adsorption of reactive species.
- In the IBAD process, the relative ratio of bombarding ions to depositing atoms can be controlled.

Some possible disadvantages of ion plating are:

- Many processing parameters that must be controlled.
- Contamination is desorbed from surfaces by plasma-surface interactions.
- Contamination is "activated" in the plasma and can become an important process variable.
- To bombard growing films of electrically insulating materials from a plasma, the surfaces must either attain a high self-bias or must be biased with an rf or pulsed DC potential.
- Processing and "position equivalency" can be very dependent on substrate geometry and fixturing—obtaining uniform bombardment and reactive species availability over a complex surface can be difficult.

- Bombarding gas species can be incorporated in the substrate surface and deposited film if too high a bombarding energy is used.
- Substrate heating can be excessive.
- High residual compressive growth stresses can be built into the film due to "atomic peening."
- In IBAD there is no plasma near the substrate to "activate" the reactive species so the activation is usually done using an auxiliary plasma source or in a plasma or ion source.

8.11 SOME APPLICATIONS OF ION PLATING

Ion plating is generally more complicated than vacuum evaporation, sputter deposition and arc vaporization since it requires having bombardment over complex surfaces. The ion plating technique is used where the advantages of ion plating are desired. The most commonly use ion plating configuration is that of the plasma-based version.

8.11.1 Plasma-Based Ion Plating

- Obtaining good adhesion between a film and substrate—e.g., Ag on steel for mirrors and bearings, Ag on Be for diffusion bonding,[58][59] Ag and Pb for low shear solid film lubricants[144]
- Electrically conductive layers—e.g., Al, Ag, Au on plastics and semiconductors
- Wear and abrasion-resistant coatings—e.g., TiN, TiC_xN_y, [Ti-Al]C_xN_y, $Ti_{0.5}Al_{0.5}N$ on cutting tools,[35] dies, molds and jewelry, and CrN+Cr_2O_3 on piston rings
- Wear resistance and lubricity—CrN on piston rings
- Decorative coatings (TiN→ gold-colored deposit, TiC_xN_y → rose-colored deposit, TiC → black deposit, ZrN → brass-colored deposit)—e.g. on hardware, jewelry, guns,[145] cutlery

- Corrosion protection—e.g., Al on U,[146] mild steel[133] and Ti ; C and Ta on biological implants
- Deposition of electrically conductive diffusion barriers—e.g., HfN & TiN on semiconductor devices
- Deposition of insulating films - e.g. Al_2O_3, SiO_2, ZrO_2
- Deposition of optically clear electrically conducting layers (indium-tin-oxide ITO)[147]
- Deposition of permeation barriers on webs[148]

Ion plating has been used to coat very large structural parts with aluminum for corrosion protection often as an alternative to electroplated cadmium.[133] Ion plated coatings can also be used for depositing adherent layers as a base for further deposition by other techniques such as electroplating[149] and painting.[133][150]

Ion plating using film ions is used to fill vias and trenches on semiconductor surfaces by sputter deposition. By postvaporization of the film atoms and accelerating the ions to the surface they arrive with a more near normal angle-of-incidence than if they were sputter deposited without ionization and acceleration.[56][57] Figure 6-11 shows the effect of ion bombardment on producing TiN as determined from electrical resistivity measurements.[36]

8.11.2 Vacuum-Based Ion Plating (IBAD)

- Dense optical coatings—e.g., high index of refraction (ZrO_2, TiO_2, ZnS), low index of refraction (SiO_2, MgF_2)
- Compound materials of specific composition by limiting the availability of a reactive species—e.g., CuO, Cu_2O[38]
- Corrosion protective coatings[151]

8.12 A NOTE ON IONIZED CLUSTER BEAM (ICB) DEPOSITION

The Ionized Cluster Beam (ICB) deposition process was reported in the early 1970s.[152][153] It was proposed that clusters of atoms (1000 or so) can be formed by adiabatic cooling by evaporation through a nozzle

into a vacuum and that the clusters could be charged and accelerated to high velocities. The deposition process was initially called an ion plating process.[154] The name was then changed to Ion Cluster Beam (ICB) and then to Partially Ionized Beam (PIB) deposition. Many metals were reported to form clusters. However, other investigators have been unable to reproduce the formation of clusters by nozzle expansion for most of the materials used and today it is believed that the changes in film properties seen in many of the ICB investigations was due to the ionization and acceleration of atoms of the film material. Some materials, such as zinc, can form clusters by gas phase nucleation in dense metal vapor clouds.[155] Clusters can also be formed by evaporation into a gas cell (gas evaporation).

8.13 SUMMARY

Under proper conditions, films deposited by ion plating have good adhesion, good surface coverage, and are more dense than films deposited by either vacuum deposition or sputter deposition. Generally, it is found that concurrent bombardment increases the reaction probability, therefore the materials deposited by reactive ion plating can be made stoichiometric more easily than with reactive sputter deposition or reactive vacuum evaporation. Therefore, in reactive deposition good stoichiometry can be attained at low temperatures due to bombardment-enhanced chemical reactions. On three dimensional objects the "front-to-back" coverage is good and the affect of angle-of-incidence of the depositing flux on film growth is negated by the bombardment.

However it has been found that if the bombarding species is too energetic and the substrate temperature is low, high gas incorporation, high defect concentrations, high residual compressive stress and the formation of voids can lead to poor quality films.

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9

Atomistic Film Growth and Some Growth-Related Film Properties

9.1 INTRODUCTION

Atomistic film growth occurs as a result of the condensation of atoms that are mobile on a surface ("adatoms"). The properties of a film of a material formed by any PVD process depends on four factors that affect film growth and properties, namely:

- Substrate surface condition—e.g., surface morphology (roughness, inclusions, particulate contamination), surface chemistry (surface composition, contaminants), surface flaws, outgassing, preferential nucleation sites, and the stability of the surface
- Details of the deposition process and system geometry—e.g., distribution of the angle-of-incidence, of the depositing adatom flux, substrate temperature, deposition rate, gaseous contamination, and concurrent energetic particle bombardment
- Details of film growth on the substrate surface—e.g., surface mobility of the depositing adatoms, nucleation, interface formation, interfacial flaw generation, energy input to the growing film, concurrent bombardment, growth

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morphology of the film, gas entrapment, reaction with deposition ambient (including reactive deposition processes), changes in the film and interfacial properties during deposition

- Post-deposition processing and reactions—e.g., reaction of the film surface with the ambient, thermal or mechanical cycling, corrosion, interfacial degradation, deformation (e.g., burnishing, shot peening) of soft surfaces, overcoating ("topcoat")

In order to have consistent film properties each of these factors must be reproducible.

Technological or engineering surfaces are terms that can be applied to the "real" surfaces of engineering materials and are discussed in Ch. 2. These are the surfaces on which films must be formed. Invariably the real surface differs chemically from the bulk material by having surface layers of reacted and adsorbed material such as oxides and hydrocarbons. These layers, along with near-surface region of the substrate, must be altered to produce the desired surface properties. The surface chemistry, morphology, and mechanical properties of the near-surface region of the substrate can be very important to the film formation process. For example, a wear-resistant coating on a soft substrate may not function well if, under load, it is fractured by the deformation of the underlying substrate. Also, good film adhesion cannot be obtained when the substrate surface is mechanically weak, since failure can occur in the near-surface substrate material. The bulk material can influence the surface preparation and the deposition process by continual outgassing and outdiffusion of internal constituents.

The nature of the real surface depends on its formation, handling, and storage history (Ch. 2). In order to have reproducible film properties, the substrate surface must be reproducible. This reproducibility is attained by careful specification of the substrate material, in-coming inspection procedures, surface preparation and appropriate handling and storage of the material.

Some of the surface properties that affect the formation and properties of the deposited film are:

- *Surface chemistry*—affects the adatom-surface reaction and nucleation density and can affect the stability of the interface formed by the deposition.

- *Contamination* (particulate, local, uniform)—affects surface chemistry and nucleation of the adatoms on the surface. Particulate contamination generates pinholes in the deposited film.
- *Surface morphology*—affects the angle-of-incidence of the depositing atoms and thus the film growth. Geometrical shadowing of the surface from the depositing adatom flux generates porosity in the coating.
- *Mechanical properties*—affects film adhesion and deformation under load
- *Outgassing*—affects nucleation, film porosity, adhesion and film contamination
- *Homogeneity* of the surface—affects uniformity of film properties over the surface

In particular, the surface morphology can have an important effect on the film properties. Figure 9-1 shows an example of the effect of surface morphology and particulate contamination has on surface coverage, film density, and porosity. Also, the surface morphology can affect the average angle-of-incidence of the adatom flux on a specific area, which has a large effect on the development of the columnar morphology and properties of the atomistically deposited films.

Surface preparation is the process of preparing a surface for the film/coating deposition process and can be comprised of surface modification (Sec. 2.6) and cleaning (Ch. 12). Care must be taken to ensure that the preparation process does not change the surface in an undesirable or uncontrolled manner. One objective of any surface preparation procedure is to produce as homogeneous a surface as possible.

Each of the PVD techniques and its associated deposition system, parameters and fixturing, has unique aspects that affects film growth. For example, the vacuum deposition environment can provide a deposition environment where the contamination level and gaseous particle fluxes incident on a surface can be carefully controlled and monitored. The plasma environment provides ions that can be accelerated to high energies to allow concurrent energetic particle bombardment of the growing film to allow modification of the film properties. The plasma deposition environment is mostly composed of uncharged gaseous species. In "high-pressure plasmas" (> 5 mTorr), gas phase collision will tend to "thermalize" and scatter energetic species as they pass through the environment. In

"low-pressure plasmas" (<5 mTorr) there will be little gas scattering and thermalization. In reactive deposition the plasma "activates" reactive gases making them more chemically reactive. This activation occurs by: (1) disassociation of molecules, (2) excitation of atomic and molecular species, (3) ionization of species and (4) generation of new species. In addition, the plasma will: (1) emit ultraviolet radiation which can aid in chemical reaction and surface energetics by photoabsorption and (2) re-combination and de-excitation of plasma species at the surface which will provide a flux of energy to the surface.

An important factor in the growth of the atomistically deposited film is the angular distribution (angle-of-incidence) of the impinging atom flux. This angular distribution will vary for each deposition geometry and each type of vaporization source. When the vapor source is a point source, and the source-substrate distance is large, the angular distribution at a point on the substrate surface is small but very non-isotropic with position. If the vapor originates from a large area, the angular distribution at a point on the substrate will be large and often non-isotropic with position. The flux and flux distribution can be made more homogeneous by using appropriate moving fixtures (Sec. 3.5.5).

Reactive deposition is the formation of a film of a compound either by co-deposition and reaction of the constituents or by the reaction of a deposited species with the ambient gaseous environment. If the reacting species form a volatile compound, etching results. If they form a non-volatile species, a compound film is formed. Reactively deposited films of oxides, carbides, nitrides and carbonitrides are commonly used in the optics, electronics, decorative and mechanical applications. Stoichiometry is the numeric ratio of elements in a compound and a stoichiometric compound is one that has the most stable chemical bonding. Many compounds have several stable stoichiometries; e.g., FeO (ferrous oxide - black) and Fe_2O_3 (ferric oxide - red). The stoichiometry of a deposited compound can depend on the amount of reactants that are available and/or the reaction probability of the deposited atoms reacting with the ambient gas before the surface is buried.

In quasi-reactive deposition, a compound material is vaporized in a partial pressure of reactive gas that aids in replacing the species lost in the transport from the vaporization source to the substrate. Quasi-reactive deposition typically does not require as high a concentration of reactive gas as does reactive deposition since most of the reactive gas is supplied from the vaporizing source material.

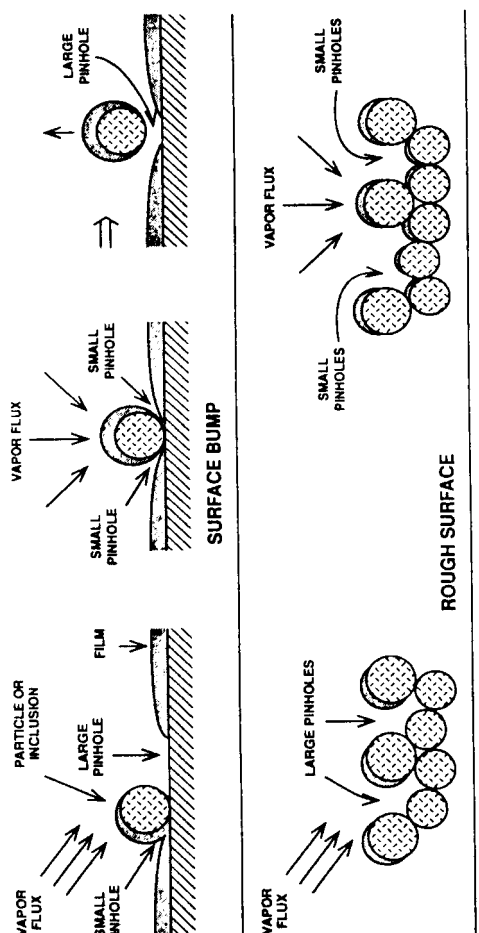


Figure 9-1. Surface morphology effects on surface coverage and pinhole formation.

The stages of film growth are:

- Condensation and nucleation of the adatoms on the surface
- Nuclei growth
- Interface formation
- Film growth—nucleation and reaction with previously deposited material
- Post-deposition changes due to post-deposition treatments, exposure to the ambient, subsequent processing steps, in-storage changes, or in-service changes

All of these stages are important in determining the properties of the deposited film material.[1–4] It should be noted that changes in film properties can occur during the deposition process. This may be due to heating of the film and substrate during the deposition.

9.2 CONDENSATION AND NUCLEATION

Atoms which impinge on a surface in a vacuum environment are either reflected immediately, re-evaporate after a residence time or condense on the surface. The ratio of the condensing atoms to the impinging atoms is called the sticking coefficient. If the atoms do not immediately react with the surface, they will have some degree of surface mobility over the surface before they condense. The mobile atoms on the surface are called adatoms. Re-evaporation is a function of the bonding energy between the adatom and the surface, the surface temperature, and the flux of mobile adatoms. For example, the deposition of cadmium on a steel surface having a temperature greater than about 200°C will result in total re-evaporation of the cadmium, whereas at a lower substrate temperature, a film will form.

9.2.1 Surface Mobility

The mobility of an atom on a surface will depend on the energy of the atom, atom-surface interactions (chemical bonding), and the temperature of the surface. The mobility on a surface can vary due to changes in chemistry or crystallography. The different crystallographic planes of a

surface have different surface free energies which affect the surface diffusion (e.g. for fcc metals the surface free energy of the (111) surface is less than that of the (100) surface and the surface mobility of an adatom is generally higher on the (111) surface than on the (100) surface). This means that different crystallographic planes will grow at different rates during adatom condensation. Various techniques have been developed to study surface mobility and the surface diffusion rate of adatoms on a surface.[5]–[9] Adatom surface mobility can be increased by low energy ion bombardment during deposition and this effect is used in the low temperature growth of epitaxial films.[10]

9.2.2 Nucleation

Atoms condense on a surface by losing energy and bonding to other atoms. They lose energy by chemical reaction with the substrate surface atoms, finding preferential nucleation sites (e.g., lattice defects, atomic steps, impurities), collision with other diffusing surface atoms and collision with adsorbed surface species. The condensation of atoms and dimers on a perfect surface has been treated by rate theory.[11][12]

The condensing atoms react with the surface to form atom-to-atom chemical bonds. The chemical bonding may be by metallic (homopolar) bonding where the atoms share orbital electrons, by electrostatic (coulombic, heteropolar) bonding where ions are formed due to electron loss/gain, or by electrostatic attraction (van der Waals forces) due to polarization of atoms. If the atom-atom interaction is strong, surface mobility is low and each surface atom can act as a nucleation site. If the resulting chemical bond between the condensed atom and the surface is strong, the atom is said to be chemisorbed. In some cases, the chemisorbed atom displaces the surface atoms giving rise to a "pseudomorphic" surface structure. The bonding energy of atoms to surfaces can be studied by thermal desorption techniques[13] and the crystallographic structure of the chemisorbed species can be studied by LEED, RHEED and field ion microscopy. The chemisorption energy for some materials on clean surfaces are shown in Table 9-1.

The bonding between a metal atom and an oxide surface is proportional to the metal-oxygen free energy of formation[14,15] with the best adhesion produced by the formation of an intermediate mixed-oxide interfacial layer. In many instances, the surface composition can differ significantly from that of the bulk of the material and/or the surface can have an

nonhomogeneous composition. An example is the glass-bonded alumina ceramics shown in Fig. 2-2. Film atoms prefer to nucleate and react with the glassy (Si-O) phase and if this material is leached from the surface during surface preparation, the film adhesion suffers.[16] Preferential sputtering of a compound or alloy substrate surface can change the surface chemistry. For instance, sputtering of an Al_2O_3 surface preferentially removes oxygen, leaving an Al-rich surface.[17] Surface contamination can greatly influence the nucleation density, interfacial reactions and nuclei orientation.[18]–[20] When depositing a binary alloy, the two materials may react differently with the surface giving phase segregation on the surface.[21]

Table 9-1. Chemisorption Energies of Atoms on Surfaces

Rb on W = 2.6 eV	Ni on Mo = 2.1 eV	
Cs on W = 2.8 eV	Ag on Mo = 1.5 eV	
B on W = 6.1 eV	Au on W = 3.0 eV	
N_2 on Fe = 3.0 eV	O_2 on Mo = 7.5 eV	1 eV/atom = 23 kcal/mole

If the adatom-surface interaction is weak, the adatom will have a high surface mobility and will condense at preferential nucleation sites where there is stronger bonding either due to a change in chemistry (elemental or electronic) or an increase in coordination number (e.g., at a step). Preferential nucleation sites can be: morphological surface discontinuities such as steps or scratches, lattice defects in the surface such as point defects or grain boundaries, foreign atoms in the surface, charge sites in insulator surfaces, or surface areas which have a different chemistry or crystallographic orientation.

Steps on a surface can act as preferential nucleation sites. For example, gold deposited on cleaved single-crystal NaCl or KCl show preferential nucleation on cleavage steps.[22][23] Steps on Si, Ge, and GaAs single crystal surfaces can be produced by polishing at an angle of several degrees to a crystal plane. This procedure produces an "off-cut" or "vicinal" surface[24] comprised of a series of closely spaced steps. These steps aid in dense nucleation for epitaxial growth of GaAs on Si[25] and $Al_xGa_{1-x}As$ on GaAs[26] by low temperature MOCVD.

Lattice defects can act as preferential nucleation sites. For example, amorphous carbon films have a high density of defects which act as nucleation sites for gold deposition.[27] When depositing adatoms on electrically insulating substrates, charge sites on the surface can act as preferential nucleation sites.[28][29] Electron irradiation,[30] UV radiation, and ion bombardment can be used to create charge sites.

Mobile surface adatoms can nucleate by collision with other mobile surface species to form stable nuclei. Thus the nucleation density can depend on the deposition (arrival) rate. For example, in the deposition of silver on lead it has been shown that at a deposition rate of 0.1 nm/min the silver is completely re-evaporated, while at 10 nm/min the atoms are completely condensed.[31] When depositing silver on glass, improved adhesion can sometimes be obtained by a rapid initial deposition rate, to give a high nucleation density by collision, followed by a lower rate to build up the film thickness.

Mobile surface species can react with adsorbed surface species such as oxygen. For example, chromium deposition immediately after oxygen plasma cleaning of glass, generally results in improved adhesion compared to a glass surface which has been oxygen-plasma cleaned and allowed to sit in the vacuum for a time before deposition. This is due, in part, to the adsorption of oxygen on glass, increasing the nucleation density of deposited atoms.[32] The adsorption of reactive species can have an important effect in reactive deposition processes.[33]

Unstable surfaces can change their nature when atoms are added to the surface. For example, the condensed atom may interact with the surface lattice and cause atomic rearrangement such that a "pseudomorphic" surface is formed which presents a different surface to atoms subsequently deposited. Some polymers, particularly non-glassy polymers (i.e., those above their glass transition temperatures), have surfaces into which the depositing atom will "sink" and possibly even nucleate below the polymer surface.[34] Polyethylene and polypropylene are examples of polymers which are non-glassy at room temperature.

Nucleation Density

In general, the number of nuclei per unit area or nucleation density should be high in order to form a dense film, obtain complete surface coverage at low film thickness, and have good contact to the surface. The nucleation density and growth behavior can vary with different substrate

locations due to phase distribution[35] or crystallographic orientation of the substrate surface.[36] The variation of nucleation density and associated subsequent film growth can result in film property variations over the surface.[37][38]

The relative and/or absolute nucleation density can be determined by a number of techniques including:

- Optical density of the deposited film as a function of mass deposited
- Behavior of the Thermal Coefficient of Resistivity (TCR)
- Transmission Electron Microscopy (TEM)[39] and Ultrahigh Vacuum TEM[40]
- Auger Electron Spectroscopy (AES)[41,42]
- Low Energy Electron Diffraction (LEED)[43] and RHEED
- Work function change[44]
- Field ion microscopy (FIM)
- Scanning Electron Microscopy (SEM)
- Scanning Tunneling Microscopy (STM)[45][46]
- Atomic Force Microscopy (AFM)[47][48]

The optical density (OD) of a film formed by depositing a given amount of material can be used to measure the comparative nucleation density on transparent substrate materials. The optical density is defined as the logarithm of the ratio of the percent of visual light transmitted through the substrate to the percent of visual light transmitted through the metallized substrate. A good electrical conductor having a high density is visually opaque when the film thickness is about 1000 Å. Optical density comparison of films deposited on glass is often a good "quick-check" on process reproducibility and can be measured either by eye or with a "densitometer."

The temperature coefficient of resistance (TCR) of a material is the manner in which the resistance changes with temperature. For metals, the TCR is positive (i.e., the resistance increases with temperature) while for dielectrics the TCR is negative (i.e., the resistance goes down with temperature). The TCR of very thin metal films on electrically insulating substrates depends on the growth of the nuclei. Isolated nuclei result in a negative TCR (increasing temperature $\longrightarrow$ decreasing resistance) due to the thermally activated tunneling conduction between nuclei.[49] Connected

nuclei, which form a continuous film, have a positive TCR as would be expected in a metal. Thus TCR measurements can be used to provide an indication of nucleation density and growth mode by determining the nature of the TCR as a function of the amount of material deposited.

Using Low Energy Electron Diffraction (LEED) it has been shown that very low coverages of contamination can inhibit interfacial reaction and epitaxial growth.[19] Field Ion Microscopy (FIM) has been used to field evaporate deposited material and observe the "recovered" substrate surface. Using this technique to study the deposition of copper on tungsten it was shown that electroplating results in interfacial mixing similar to high temperature vacuum deposition processing.[50]

Modification of Nucleation Density

There are a number of ways to modify the nucleation density of depositing atoms on substrate surfaces including:

- Change the deposition temperature

  increasing—increases reaction with the surface; increases surface mobility

  decreasing—decreases surface mobility
- Increase the deposition rate to increase collision probability of the adatoms
- Change the surface chemistry to make the surface more reactive—e.g., cleaning,[51] oxygen treatment of polymer surfaces[52]
- Sensitizing the surface by the addition of "nucleating agents"
- Generation of nucleation sites on the surface—e.g., lattice defects, charge sites on insulators[53] by
  - © energetic particle bombardment to produce lattice defects[55]-[61]
  - © incorporation of species into the surface by ion implantation[62][63] or chemical substitution
  - © electron bombardment[64]–[67]—charge centers on insulator surfaces
  - © photon bombardment[68]—charge centers on insulator surfaces

- Co-deposition or absorption of reactive species
- Surface morphology—roughening or smoothing
- Creation of a new surface—"basecoat" or "glue layer"

Adsorbed or co-deposited reactive species can affect the surface chemistry and thus the nucleation of the deposited species. The presence of adsorbed oxygen or oxygen in a plasma or bombarding oxygen ion beam during deposition has been shown to aid in the adhesion of gold[69]–[75] and oxygen-active film materials,[76]–[80] to oxide substrates. The increased adhesion is attributed to the increased nucleation density. In the case of plasma deposition such as Plasma Enhanced Chemical Vapor deposition (PECVD) from a vapor precursor, the radicals, unique species, and excited species formed in the plasma may play an important role in adsorption and deposition from a gaseous precursor. For example, in the deposition of silicon from silane by PECVD, it has been proposed that the formation of disilane and trisilane in the plasma and its adsorption on the surface along with low energy particle bombardment, is important to the low temperature–high rate deposition of amorphous silicon.[81][82][88]

Surface roughness can also play an important role in nucleation density. The 96% alumina, shown in Fig. 2-2, has a surface roughness that looks like a field of boulders several microns in diameter. Deposition on such a surface results in a high nucleation density on the tops of the boulders and a lower nucleation density on the sides and in the pores. Flowed glass surfaces, on the other hand, are smooth and the nucleation density is uniform over the surface.

Basecoats can provide a new and better surface for the deposition of the desired material.[76][83] This is often done in the metallization systems used in microelectronics and for interconnects in integrated circuit technology. In these cases, a material is deposited on the oxide/semiconductor surface that forms a desirable oxide interface (e.g., Ti or Cr). Then a surface layer is deposited which alloys with the first layer and provides the desired electrical conductivity, bondability, corrosion resistance, etc (e.g., Au, Cu, Ag). The new surface can also be used to smooth or "planarize" the initial surface (e.g., a "flowed" basecoat layer).

9.2.3 Growth of Nuclei

Nuclei grow by collecting adatoms which either impinge on the nuclei directly or migrate over the surface to the nuclei. Three different

types of nucleation mechanisms have been identified depending on the nature of interaction between the deposited atoms and the substrate material:[2][4][84] (*i*) the van der Merwe mechanism leading to a monolayer-by-monolayer growth. (*ii*) the Volmer-Weber mechanism characterized by a three dimensional nucleation and growth. (*iii*) the Stranski-Krastanov (S-K) mechanism where an altered surface layer is formed by reaction with the deposited material to generate a strained or pseudomorphic structure, followed by cluster nucleation on this altered layer. The S-K nucleation is common with metal-on-metal deposition and at low temperatures where the surface mobility is low.[85][86] The conditions for these types of growth is generally described in term of thermodynamics and surface energy considerations.[87]–[90]

Often the adsorption is accompanied by surface reconstruction, surface lattice strain, or surface lattice relaxation which change the lattice atom spacing or the surface crystallography to produce a pseudomorphic structure.[91][92] The interaction of the depositing material with the surface can form a structure on which subsequent depositing atoms nucleate and grow in a manner different from the initially depositing material. This may alter the subsequent film structure. For example, a unique beta-tantalum structured film is stabilized by deposition on an as-grown tantalum silicide interfacial material.[93]

Isolated nuclei on a surface can grow primarily laterally over the surface (wetting growth) or primarily normal to the surface (de-wetting growth) to form a continuous film.[94] The higher the nucleation density and the more the wetting-type growth the less the amount of material needed to form a continuous film. Examples of wetting-type growth, are: Au on Cu, Cr and Fe on W-O surfaces,[94] and Ti on SiO_2; and of de-wetting growth are Au on C, Al_2O_3, or SiO_2. Growth and coalescence of the nuclei can leave interfacial voids or structural discontinuities at the interface, particularly if there is no chemical interaction between the nuclei and the substrate material, and dewetting growth occurs.

In cases where there is little chemical interaction between the nucleating atoms and the substrate, the isolated nuclei grow together producing the so-called island-channel-continuous film growth stages.[95] Before coalescence, the nuclei can have a liquid-like behavior that allows them to rotate and align themselves crystallographically with each other giving an oriented overgrowth.[96][97] The nucleation of deposited atoms on surfaces can be studied *in situ* using ultrahigh-vacuum transmission electron microscopy (UHV-TEM).

Agglomeration of nuclei occurs when the temperature of the nuclei is high enough to allow atomic diffusion and rearrangement such that the nuclei "ball-up" to minimize the surface area. Fine particles, formed by agglomeration of indium particles on polymer surfaces, resemble chromium optically, and are used for decorative purposes. Agglomeration of evaporated gold films is increased at high deposition rates, at high substrate temperatures and in high-rate electron beam evaporation.[98] Gold is often used for replication in electron microscopy and agglomeration of pure gold can be a problem. Gold alloys, such as 60Au:40Pd, are used to reduce the agglomeration tendencies and provide better replication. Agglomeration is promoted after deposition if there is appreciable columnar growth (high surface area), high residual stress in the film, and/or the film is heated.

Where there is strong interaction between the adatoms and the substrate but little diffusion or compound formation, the crystal orientation of the deposited material can be influenced by the substrate crystallographic orientation producing a preferential crystallographic orientation in the nuclei. This type of oriented overgrowth is called epitaxial growth. Lattice mismatch between the nuclei and the substrate at the interface may be accommodated by lattice strain or by the formation of "misfit" dislocation networks.[99] Under proper conditions a single crystal epitaxial film can be grown. This is often the goal in molecular beam epitaxy (MBE) and Chemical Vapor Deposition (CVD) (or Vapor Phase Epitaxy) of semiconductor thin films. In the growth of semiconductor materials, it is desirable to form an interface which is defect free so that electronically active sites are not generated. Such an interface can be formed if there is lattice parameter matching between the deposited material and the substrate, or if the deposited material is thin enough to allow lattice strains to accommodate the lattice mismatch without producing dislocation networks. This latter condition produces a "strained layer superlattice" structure.[100]

At the other extreme of growth are amorphous materials where rapid quenching, bond saturation, limited diffusion, and the lack of substrate influence results in a highly disordered material. Comparison between amorphous materials formed by co-evaporation and those formed by rapid quenching show some indication of a lower degree of short range ordering in the co-deposited material, as indicated by the lower crystallization temperature and lower activation energy for crystallization than in the low temperature deposited films.[101] Since amorphous films have no grain boundaries, they are expected to show lower diffusion rates than films that

have grain boundaries, since grain boundary diffusion rates are higher than bulk diffusion rates. Amorphous conductive material, such as $W_{75}Si_{25}$[102] have been proposed as a diffusion barrier film in semiconductor metallizations. Nucleation on a surface can be modified from a disordered state to an ordered state by carefully controlled concurrent ion bombardment.[103]

9.2.4 Condensation Energy

At high deposition rates, the condensation energy can produce appreciable substrate heating.[104][105] When a thermally vaporized atom condenses on a surface it releases energy from several sources including:

- Heat of vaporization or sublimation (enthalpy of vaporization)—a few eV per atom
- Energy to cool to ambient—depends on heat capacity and temperature change
- Energy associated with reaction—may be exothermic where heat is released or endothermic where heat is adsorbed
- Energy released on solution—heat of solution

If the kinetic energy of the depositing adatom is greater than thermal energy acquired on vaporization, either due to being vaporized by sputtering (and not thermalized), or being accelerated as an ion (film ion), the kinetic energy that it releases on condensation will be greater than thermal. If the depositing species is excited or ionized, it also releases the excitation energy or the ionization energy on de-excitation or recombination. In these situations the energy released also includes:

- Excess kinetic energy
- Excitation energy—if an excited species
- Ionization energy—if an ionized species

The thermal vaporization energy for gold is about 3 eV per atom[106] and the kinetic energy of the vaporized atom is about 0.3 eV per atom. Thus the kinetic energy is only a small part of the energy being released during deposition. However it has been shown, using mechanical velocity filters, that the kinetic energy of the depositing gold particles is important to the film structure, properties, and annealing behavior.[107]

9.3 INTERFACE FORMATION

The depositing film material may diffuse and react with the substrate to form an "interfacial region." The material in the interfacial region has been called the "interphase material" and its properties are important to the adhesion, electrical, and electronic properties of film-substrate systems. In particular, the development of ohmic contacts to semiconductor materials is very dependent on the interface formation process.[108][109] The type and extent of the interfacial region can change as the deposition process proceeds or be modified by post-deposition treatments. Interfacial regions are categorized as:[110]

- Abrupt
- Diffusion
- Compound (also requires diffusion)
- Pseudodiffusion (physical mixing, implantation, recoil implantation)
- Reactively graded
- Combinations of the above

Figure 9-2 schematically shows the types of interfacial regions.

9.3.1 Abrupt Interface

The abrupt interface is characterized by an abrupt change from the film material to the substrate material in a distance on the order of the atomic spacing (i.e., 2–5 Å) with concurrent abrupt changes in material properties. This type of interface is formed when there is no bulk diffusion and generally signifies weak chemical reaction between the depositing atoms and the substrate, a low deposition temperature, surface contamination, or no solubility between the film and substrate materials. Some systems such as silver on iron and indium or gallium on GaAs[111] have no solid solubility and an abrupt interface is formed. The formation of this type of interfacial region generally means that the nucleation density is low and the film will have to grow to appreciable thickness before the film becomes continuous. This results in the formation of interfacial voids. Typically the adhesion in this system is low because the interfacial voids provide an easy fracture path.

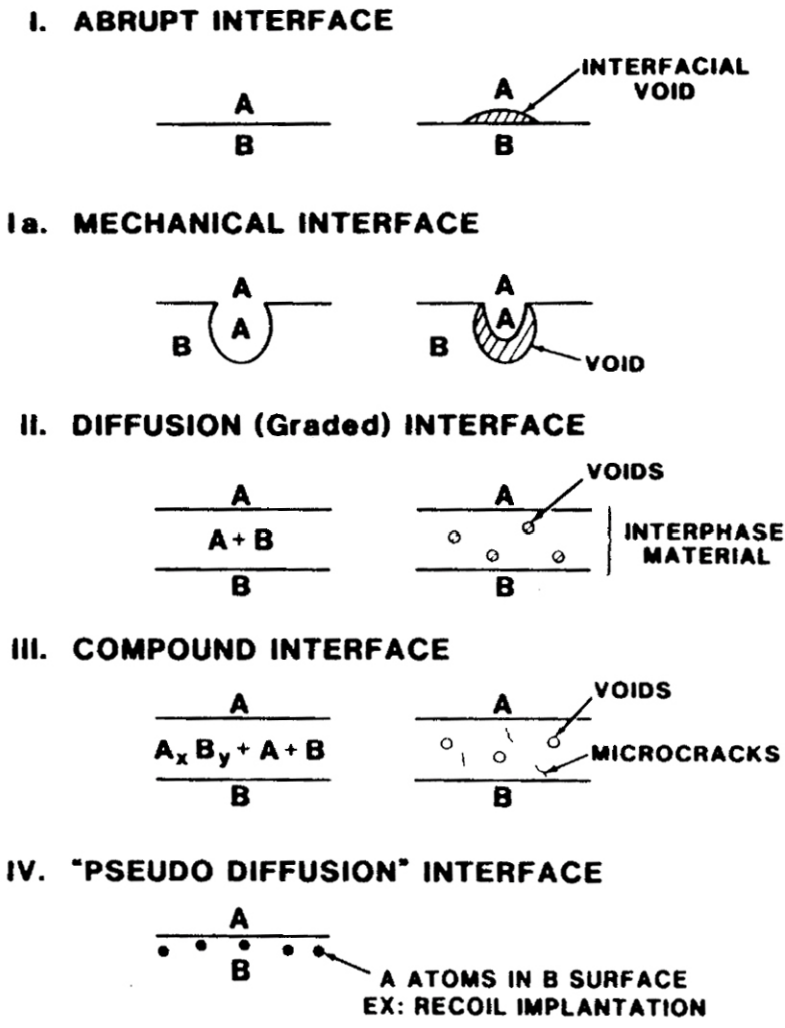


Figure 9-2. Types of interfacial regions.

Mechanical Interlocking Interface

The mechanical interface is an abrupt interface on a rough surface. If the deposited material forms a conformal coating, the rough surface is "filled-in" to give mechanical interlocking. The strength of the interface depends on the mechanical properties of the materials. To fracture along the interface requires following a torturous path with changing stress

tensors and the adhesion of the film to the surface can be high. Surfaces can be made rough to increase the degree of mechanical interlocking.[112] The adhesion of this structure may be limited by the deformation properties of the materials involved. If the roughness is not "filled-in," the adhesion will be low due to the lack of contact and interfacial voids. The "filling-in" of the roughness can be aided by having a dispersed adatom flux distribution, concurrent energetic particle bombardment, or high surface mobility of the deposited material.

9.3.2 Diffusion Interface

The diffusion interface is characterized by a gradual change or gradation in composition across the interfacial region with no compound formation. The diffusion interface is formed when there is mutual solid solubility between the film and substrate material and the temperature and time are sufficient to allow diffusion to occur.[113][114] This type of interfacial system is often found in metallic systems. For example, the study of the vacuum deposition of copper on aluminum shows that diffusion occurs at temperatures as low as 120 K giving a diffusion-type interface.[115] The diffusion interface provides a gradation in materials properties from the film to the substrate and this graded interface can be important in obtaining good adhesion or crystalline orientation. If contamination is present on the surface, diffusion can be suppressed or the diffusion will not occur.[116][117]

The extent of diffusion in the interface depends on time and temperature. Differing diffusion rates of the film and substrate materials can create porosity in the interfacial material. Porosity formed by this mechanism is called Kirkendall porosity. This porosity can weaken the interfacial material and provide an easy fracture path for adhesion failure. The diffusion interface is generally conducive to good adhesion, but if the reaction region is too thick, the development of porosity can lead to poor adhesion.

In some cases, diffusion barriers are used at the interface to reduce diffusion.[118][119] For example, W+Ti or the electrically conductive nitride, TiN, is used as a diffusion barrier in silicon metallization to inhibit aluminum diffusion into the silicon during subsequent high temperature processing. This layer also increases the surface mobility of the aluminum adatoms allowing better filling of surface features such as vias. Barrier layers, such as tantalum, nickel, and Ni +Pd alloys, are used to prevent diffusion and reaction in metallic systems. For example, a nickel or Ni +

Pd alloy layer is used to prevent diffusion of zinc from brass during the sputter deposition of a TiN decorative coating on the brass.[120] The presence of compound-forming species in the depositing material reduces the diffusion rate.[121] Alternatively, materials can be alloyed with the film material to reduce diffusion rates.[122]

In high temperature processing, the substrate material near the interface can be weakened by the diffusion of a constituent of the substrate into the depositing film material. For example, the diffusion of carbon from high-carbon tool steel, during high temperature deposition, forms a weak "eta phase" at the interface.[123] Conversely the diffusion from the substrate can result in increased adhesion. For example, it has been shown that in the deposition of carbides on oxide surfaces, the oxygen intermixes and reacts with the carbide material producing a "keying" action.[124]

9.3.3 Compound Interface

Diffusion, along with chemical reaction, forms a compound interfacial region. The compounds formed are often brittle, and high stresses are often introduced due to the volumetric changes involved in forming the new phase(s). Sometimes these stresses are relieved by microcracking in the interfacial region thus weakening the interphase material. The compound interface is generally conducive to good adhesion, but if the reaction region is too thick, the development of porosity and the formation of microcracked brittle compounds can lead to poor adhesion.

The compound interface is the type of interface found in reactive systems such as oxygen-active metal films on oxide substrates, where a mixed-oxide interphase material is formed, or in intermetallic-forming metal-on-metal systems such as Au-Al[125] and Al-U.[126] In the case of Au-Al the interdiffusion and reaction form both Kirkendall voids and a brittle intermetallic phase termed "purple plague" which causes easy bond failure.[127]–[129]

When materials react, the reaction can be exothermic where energy in the form of heat is released, or endothermic where energy is taken up. Table 9-2 lists some heats of formation of various materials in forming compounds. An exothermic reaction is indicated by a negative heat of formation and an endothermic reaction is indicated by a positive heat of reaction.

In some film systems there can be an exothermic reaction such that large amounts of heat are generated after the reaction has been "triggered." Such systems are Pd-Sn, Al-Pd, and Al-Zr which have increasingly higher

"triggering" temperatures. Multilayer composite structures of these materials can be used to rapidly release heat.[130]

Table 9-2. Heat of Formation (- exothermic, + endothermic)

Ni_2Si	-11 kcal/mole	TiO_2	-218 kcal/mole
NiSi	-18	WO_3	-200
Pt_2Si	-11	MO_3	-180
PtSi	-15	Cu_2O	-40
$ZrSi_2$	-35	SiC	-15
Ta_2O_5	-500	Au in Si	-2.3 (heat of solution)
Al_2O_3	-399		
V_2O_3	-290	Ni_3C	+16
Cr_2O_3	-270	Au_2O_3	+19

It should be remembered that diffusion and reaction can continue during the deposition process particularly if an elevated deposition temperature and long deposition times are used. For example, with aluminum on platinum, an Al-Pt intermetallic is formed and as the intermetallic layer thickness increases, it removes the aluminum preferentially from grain boundaries at the Al/Al-Pt interface. This leads to void formation at the aluminum grain boundaries and the formation of "capillary voids."

As diffusion proceeds, the interfacial boundary becomes "rough."[131] Rapid diffusion can occur at grain boundaries and dislocations producing a "spiked" interfacial boundary which aids in the bonding of some coatings to surfaces but can cause shorting in semiconductor junctions. For example, the oxide "pegs" in plasma sprayed M-Cr-Al coatings on turbine blades aids in coating adhesion.[132] Ion plating with a cold substrate[133] or rapid heating and cooling can also limit diffusion in the interfacial region. When a compound is formed, generally there is a volumetric expansion. If the reaction is over a limited area, like a grain boundary, this expansion will act as a "wedge" and the stress generated will increase the reaction rate.

The interphase material formed by diffusion and reaction often contains a graded composition with properties that vary throughout the layer. If the material becomes thick, it can develop high residual stress,

voids, and microcracks that weaken the material and result in poor adhesion. The interphase material is important in film adhesion, contact resistance, and electronic "interfacial states" of metal-semiconductor contacts.[134]–[137] The mechanical properties of the interphase material can be "graded" to act as a "buffer layer" between the film and the substrate.

In the extreme, the film material can completely react with the substrate thus forming a film of the interphase material. This is usually an effect of high substrate temperature during deposition or post-deposition processing. For example, platinum on silicon can be completely reacted to form a platinum silicide electrode material on the silicon.

In the case of polymer surfaces the depositing atoms can diffuse into the surface and then nucleate, forming nuclei of the material in the subsurface region.[138] For example, in the deposition of copper on polyimide at low deposition rates (1 monolayer/min) copper nuclei are formed beneath the surface while chromium, which forms a chemical bond with the polymer chain, does not diffuse into the surface.[34] The nucleation and chemical bonding of the film atoms to the polymer surface determine the adhesion strength.[139][140]

9.3.4 Pseudodiffusion ("Graded" or "Blended") Interface

In deposition processes, an interface with a graded composition and properties can be formed by "grading" the deposition from one deposited material to the other. For example, in depositing Ti-Au or Ti-Cu metallization, the gold or copper deposition can begin before the titanium deposition has ended. This produces a graded interface similar to the diffusion interface and is called a pseudodiffusion interface. This pseudodiffusion interface can be formed between insoluble materials, such as silver and iron or osmium and gold, at low temperatures where the phases do not segregate. In soluble systems, such as Ti-Cu metallization, this method of forming the interface avoids the potential problem of oxidation of the titanium before the copper is deposited. If oxidation occurs, the adhesion between the titanium and the copper layers will be poor.[141] The pseudodiffusion type of interface can also be formed by "recoil implantation" during concurrent or subsequent ion bombardment.[142] The use of energetic ions of the film material (film-ions) allows ion implantation to form the pseudodiffusion interface.[143]

In generating the graded type of interface by co-deposition, the nucleation of the different materials can lead to phase segregation in the

graded region. For example, in co-depositing gold and tungsten, the result may not be an atomic dispersion of gold and tungsten but rather dispersed phases of gold and tungsten. This can lead to rapid development of a rough surface.[21]

9.3.5 Modification of Interfaces

Interface composition, structure and thickness can be modified by:

- Substrate surface cleaning and surface preparation
- Changing the substrate temperature and deposition time
- Introducing energy into the surface region during deposition by concurrent ion bombardment, laser heating, etc.

Surface preparation is an important factor in interface formation in that the interface reactions can be drastically modified by the presence of strongly bound contaminants such as O, C, and N, whereas weakly bound contaminants such as H_2O, CO or H, can be displaced from the surface during deposition.[144]

Ion bombardment before and during deposition can introduce defects into the surface region and diffusion can be enhanced by mechanisms similar to those found in "radiation enhanced diffusion."[145] For example, in the aluminum metallization of silicon, it has been shown that there is little diffusion of aluminum into silicon during high temperature processing if the silicon surface is undamaged. However, extensive diffusion occurs if the surface is damaged by ion bombardment prior to the deposition.[146] Bombardment allows introduction of energy into the surface without the necessity of bulk heating. In some cases, the temperature of the bulk can be kept very low by heat-sinking while the temperature of the surface region is very high giving a large temperature gradient. This limits diffusion into the surface and prevents pipe diffusion along grain boundaries.[133]

The use of accelerated ions of the film material ("film ions") allows the formation of a pseudodiffusion-type interface. Film ions can be formed by the ionization of vaporized material. This occurs naturally in arc vaporization which uses a high current of low voltage electrons to vaporize material from a cathode or anode (Ch. 7). Alternatively, ions can be formed by post vaporization of sputtered atoms[147] or evaporated atoms,[148]-[150] or in an arc-type metal ion source.[151]

A compound-containing interfacial region that consists of a graded compound-matrix material can be formed by controlling the availability of

reactive gases during reactive deposition thus forming a reactively graded interface.[152][153] For example, a TiN hard-coating on tool-steel can be deposited with a graded interfacial layer of Ti to TiN_{1-x} to TiN by controlling the availability of reactive nitrogen during deposition. This can be used to improve the adhesion of the TiN coating to the steel surface.

9.3.6 Characterization of Interfaces and Interphase Material

Generally the interfacial region and the interphase material is difficult to characterize since it usually consists of a small amount of material buried under a relatively thick film. Figure 9-3 shows the Rutherford Backscatter (RBS) analysis (Sec. 10.5.10) of tungsten metallization of a Si-Ge thermoelectric element as deposited and after a furnace treatment that diffused material at the interface. Before diffusion, the interface has no features discernible by RBS. Interdiffusion rejected the germanium and reacts to form a tungsten silicide. After extensive diffusion the interface was weakened and the adhesion failed.

In some cases, the interface can be characterized by viewing through the substrate material. For example, in the metallization of glass, viewing through the glass may show a highly reflecting surface or a darker surface. The darker surface can mean a different nucleation or reaction than the shiny surface. In a specific instance, the appearance should be uniform over the whole interface and not vary from region to region. If it varies then that indicates a non-homogeneous surface or deposition process. The appearance can be quantified by colorimetry or scatterometry. In the case of multilayer metallization, if the first layer is less than a few hundred angstroms, the appearance will be influenced by the interface with the glass and the interface between the film layers.

The beginnings of interface formation can be studied by depositing a small amount of material then studying the surface. This can be misleading because the interfacial region can be changing throughout the deposition, particularly if the deposition is done at elevated temperatures.

The interphase material that is formed in the interfacial region is important to many of the properties of the final film structure such as adhesion, mechanical properties, contact resistance, and stability. In 1988 the NSF conducted a workshop on adhesion and one of the principal determinations from the discussions was that the properties of the interphase material were poorly characterized and understood and that more knowledge was needed in this area.[154] That is still the case.

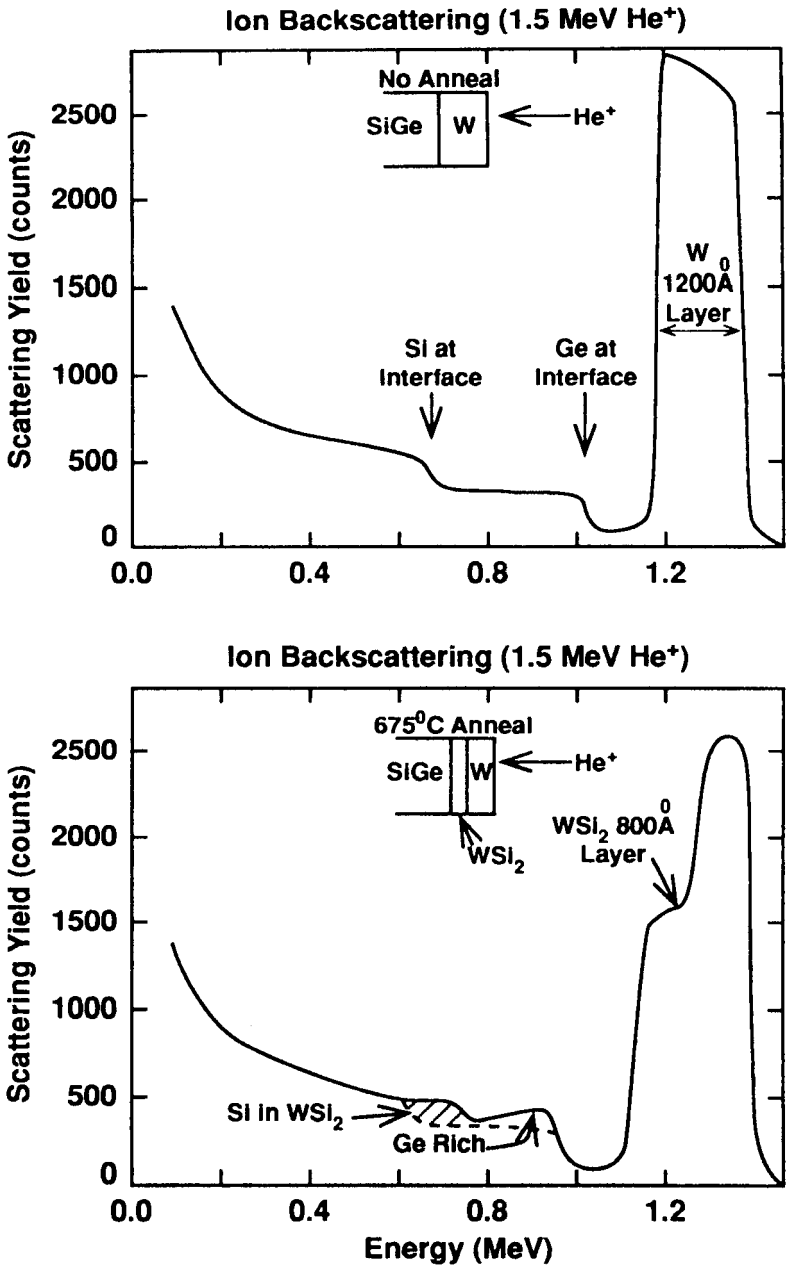


Figure 9-3. Tungsten electrode on a silicon-germanium alloy before and after post-deposition diffusion.

The interfacial material is most often characterized by fracture analysis where failure occurs in the interfacial material and after failure, the fracture surfaces can be examined. The "purple plague" failure discussed in Sec. 9.3.3 is an example. If the film is etched from the surface the interphase material can remain. For example, in the case of chromium on glass, when the chromium is removed by chemical etching, a conductive layer of chromium oxide interfacial material remains on the glass surface particularly if the deposition was done at an elevated temperature or the film has been aged before removal.

9.4 FILM GROWTH

Films grow by the continued nucleation of depositing atoms on previously deposited material[155] and the surface is continually being buried under newly depositing material. The film growth, as well as the nucleation mode, determines many film properties such as film density, surface area, surface morphology and grain size. Important aspects of film growth are:

- Substrate surface roughness—initially and as the film develops[156]
- Surface temperature—initially and as the film grows
- Adatom surface mobility[7]
- Geometrical shadowing effects (angle-of-incidence effects)
- Reaction and mass transport during deposition such as segregation effects[157] and void agglomeration[158]

Surface morphologies can vary from very smooth, such as that of a flowed glass surface, to very rough such as is found with many sintered materials. Generally, as the film grows, the surface roughness increases because some features or crystallographic planes grow faster than others. In some cases, the surface can be smoothed or "planarized" by the depositing material or the roughness can be prevented from developing. The roughness may not be uniform over the surface or there can be local areas of roughness due to scratches, vias, embedded particles, particulate contamination, etc., which lead to variations of the film properties in these areas.

9.4.1 Columnar Growth Morphology

Atomistically deposited films generally exhibit a unique growth morphology that resembles logs or plates aligned and piled together and is called a columnar morphology. Figure 9-4 shows the columnar morphology of the fracture surfaces of thick vacuum deposits of aluminum and stainless steel produced at low temperatures. This morphology develops due to geometrical effects and is found whether the material is crystalline or amorphous. The columns **are not** single crystal grains.

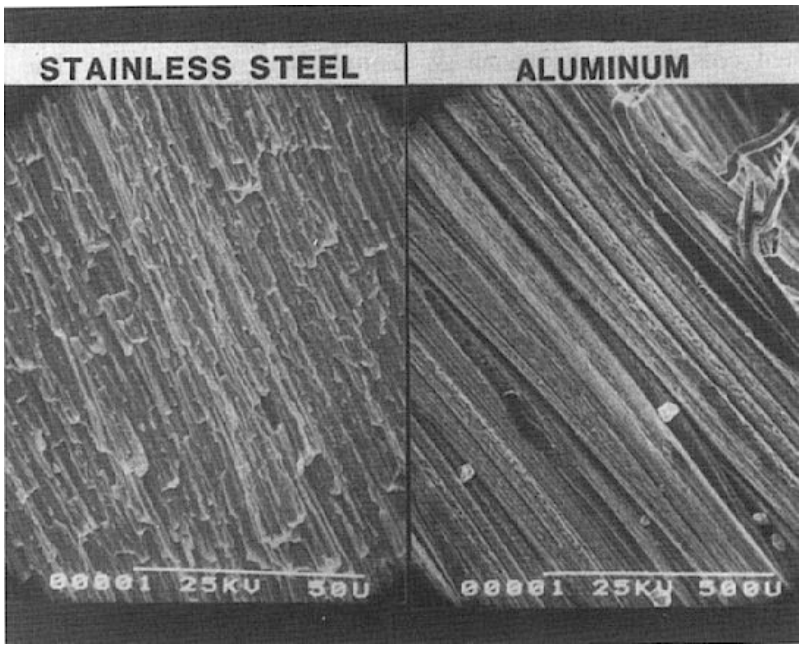


Figure 9-4. Fractographs of thick vacuum deposits of aluminum and stainless steel.

The morphology of the depositing film is determined by the surface roughness and the surface mobility of the depositing atoms with geometrical shadowing and surface diffusion competing to determine the morphology of the depositing material. When the surface is rough, the peaks receive the adatom flux from all directions and, if the surface mobility of the adatoms is low, the peaks grow faster than the valleys due

to geometrical shadowing. The shadowing effect is exacerbated if the adatom flux is off-normal so that the valleys are in "deeper shadows" than when the flux is normal to the surface. Adsorbed gaseous species decrease the adatom surface mobility while concurrent energetic particle bombardment can increase or decrease the surface mobility.

Structure-Zone Model (SZM) of Growth

Typically, the film near the interface is influenced by the substrate and/or interface material and it takes an appreciable thickness before the film establishes a particular growth mode. After a growth mode has been established the film morphology can be described by a Structure-Zone model (SZM). The structure zone model was first applied to vacuum deposited coatings by Movchan & Demchishin in 1969.[159] The MD Model is shown in Fig. 9-4. Later the structure zone model was extended to sputter-deposited films, where concurrent bombardment by high energy neutral reflected from the surface of the sputtering target can influence the film growth by Thornton[3] as shown in Fig. 9-5 and later modified by Meissier[160] to include point defect agglomeration and void coarsening with thickness.

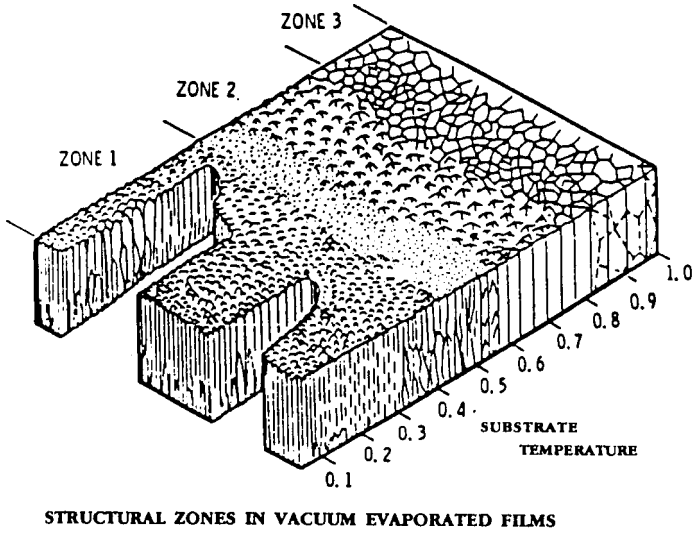


Figure 9-5. Structure zone model of vacuum evaporated condensates. (Adapted from Ref. 159)

The details of the condensation processes that determine the film morphology at low temperatures where atom mobility is low are not well understood though there are a number of factors involved.

In vacuum:

- Angle-of-incidence of the adatom flux effects—i.e., geometrical shadowing
- Ratio of deposition temperature (degrees K) to the melting temperature (degrees K) of the film material (T/T_m)
- Energy released on condensation
- Adatom surface mobility on surfaces and different crystallographic planes
- Surface roughness
- Deposition rate
- Void coalescence
- Mass transport and grain growth during deposition

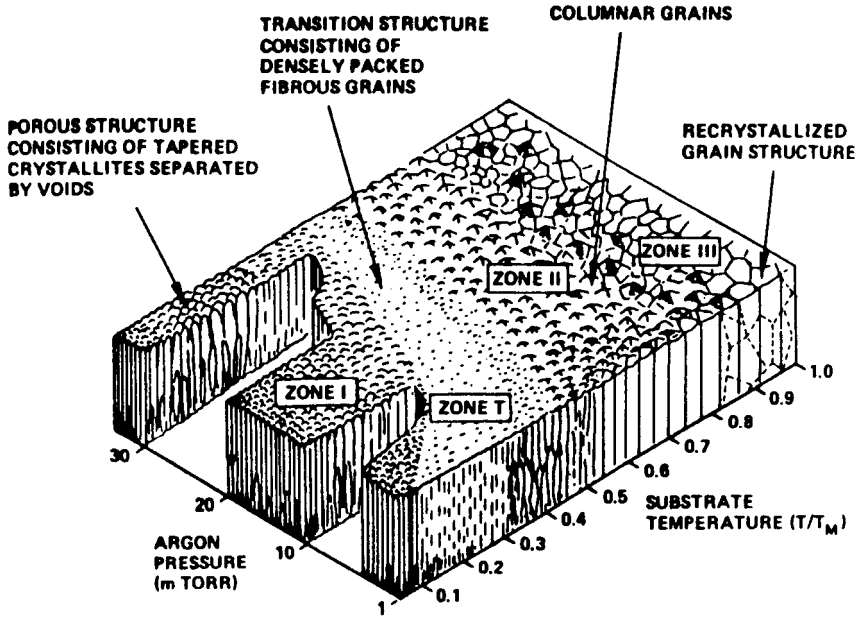


Figure 9-6. Structure zone model of sputter deposited materials (adapted from Ref. 3).

In low pressure sputter deposition, where there is bombardment by high energy reflected neutrals, and in ion plating, where there is deliberate high energy particle bombardment, additional factors include:[33][161]

- Adsorption of inert and reactive gaseous species on the growing surface
- Gas scattering of vaporized particles
- Concurrent bombardment by high energy particles

In Zone 1 of the MD model and the Thornton model, the adatom surface diffusion is insufficient to overcome the geometrical shadowing by the surface features. This gives open boundaries between the columns that are formed. This morphology produces a film with a high surface area and a film surface that has a "mossy" appearance. Higher gas pressures extend this zone to higher temperatures due to gas scattering, and decreased surface mobilities due to gas adsorption and collisions on the surface. The columnar morphology that develops has been computer modeled for depositing spheres.[162]–[166] The columns can have different shapes such as round columns for aluminum (a cubic material), and platelets for beryllium (a hexagonal close packed material) which is shown in Fig. 9-7. The columns can be microns in size but the grain size can be less than 1000 Å or even be amorphous within the columns. The columnar growth also depends on the angle-of-incidence of the atom flux.[167] The more off-normal the deposition, the more prominent is the columnar growth. Since the columnar growth is strictly a function of surface geometry, angle-of-incidence and adatom surface mobility, amorphous as well as crystalline materials show the columnar growth mode.[162][168]

The development of the columnar morphology begins very early in the film growth stage and generally becomes prominent after about 100 nm of thickness. For example, CoCr, which is a magnetic recording material that is very sensitive to film growth, can be prepared by sputter deposition or vacuum evaporation. The film consists of columnar grains with the hcp c-axis, which is the easy magnetization direction, perpendicular to the substrate surface.[169] TEM studies of the growth of sputter-deposited CoCr on NaCl at 100°C show the following stages of columnar morphology development as a function of film thickness:[170]

<5 nm → poor crystal quality - substrate effects

10 nm → good hcp with clear grain boundaries - grain size 2–8 nm, various crystallographic orientations

80 nm → well developed columnar morphology

100 nm → c-axis becomes perpendicular to growth direction (texture), grain size 15–25 nm

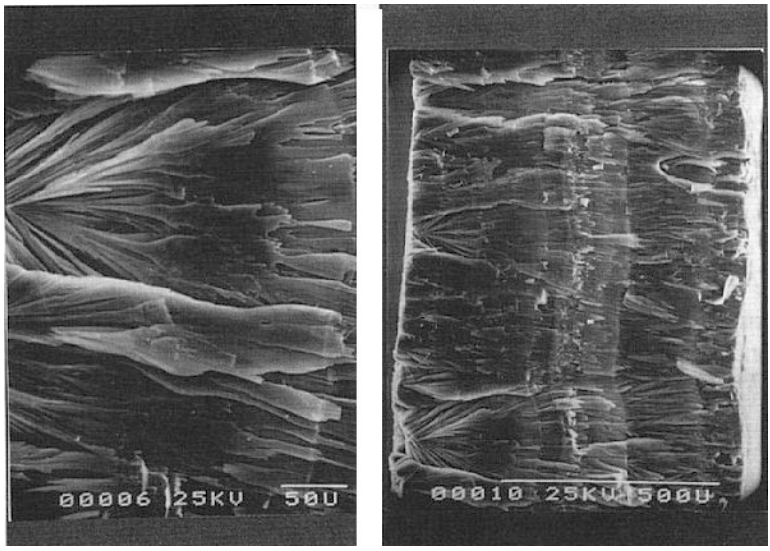


Figure 9-7. Fractograph showing the columnar morphology in vacuum deposited beryllium.

The angle-of-incidence of the adatom flux has an important effect on the columnar growth. The columnar growth is exacerbated by off-normal deposition flux orientations since now the valleys get no flux.[167][171]–[173] The off-normal angle-of-incidence can be due to a rough surface or an off-normal deposition on a smooth surface.* For an off-

*In production it was found that some gold metallization surfaces were "soft" and when wire ball bonds were applied, the ball would sink into the surface. Those particular films had an orange appearance compared to the normal gold metallization. Investigation revealed that the substrates that exhibited the problem were in the fixture such that there was a high angle-of-incidence of the depositing material giving rise to a less than fully dense columnar morphology. The problem was exacerbated by the fact that the operators were not instructed to do a "first check" characterization (Sect. 10.4.2).

normal incident flux, the columns do not grow normal to the surface but grow toward the adatom source with a change in column shape. The off-normal growth results in an even more open morphology with a lower density than the columnar morphology resulting from a normal angle-of-incidence. The off-normal incidence can vary over the surface due to local surface morphologies such as a sintered morphology (Fig. 2-2), scratches, via sidewalls, particulates, etc.

Angle-of-incidence effects can be apparent when the substrate is moved in front of the vaporization source as is the case of the use of a pallet fixture. In this case the angle-of-incidence starts very low, goes through normal incidence, then exits at a low angle-of incidence. The initial growth at the high angle can influence the growth at normal incidence.

In the zone model for sputter-deposited films Thornton introduced the Zone T. In Zone T, the coating has a fibrous morphology and is considered to be a transition from Zone 1 to Zone 2. The formation of the Zone T material is due to the energetic bombardment from reflected high energy neutrals from the sputtering target at low gas pressures. These energetic high energy neutrals erode the peaks and fill-in the valleys to some extent.

In Zone 2 the growth process is dominated by adatom surface diffusion. In this region, surface diffusion allows the densification of the intercolumnar boundaries. However the basic columnar morphology remains. The grain size increases and the surface features tend to be faceted.

In Zone 3 bulk diffusion allows recrystallization, grain growth and densification. Often the highly modified columnar morphology is detectable with the columns being single crystals of material.

9.4.2 Substrate Surface Morphology Effects on Film Growth

A columnar morphology will develop on a smooth substrate surface as it roughens with film thickness due to preferential growth of crystal planes. If the surface is not smooth, the variation in angle of incidence and the general roughness will produce a more complex morphology and generally a less dense film than on a smooth surface.[174]–[176] For example, a film grown on the surface shown in Fig. 2-2, will consist of a "microcolumnar morphology"of columns grown in films on each the individual "boulders" with varying angle-of incidence over the surface of the boulders, and a "macrocolumnar morphology" resulting from shadowing effects by the boulders. Figure 9-8 shows a nodule that developed in a

sputter-depositied chromium film due to particulate contamination on the surface. The results will be a very complicated film morphology with large local variations in film thickness and properties. If the surface has some morphology pattern such as the patterned metallization on a smooth silicon wafer, the angle-of-incidence will vary with position on the surface and differing film properties with position can be expected over the surface. For example, the film on the sidewall of a via or step can be expected to be less dense than the density of the film on the surface facing the vapor source directly[177] as shown in Fig. 1. This effect is easily demonstrated using chemical etch rate test (Sec. 10.4.3). It is important to remember that the film growth can vary over the surface due to surface inhomogeneities, angle-of-incidence variation, and variations in the process variables.

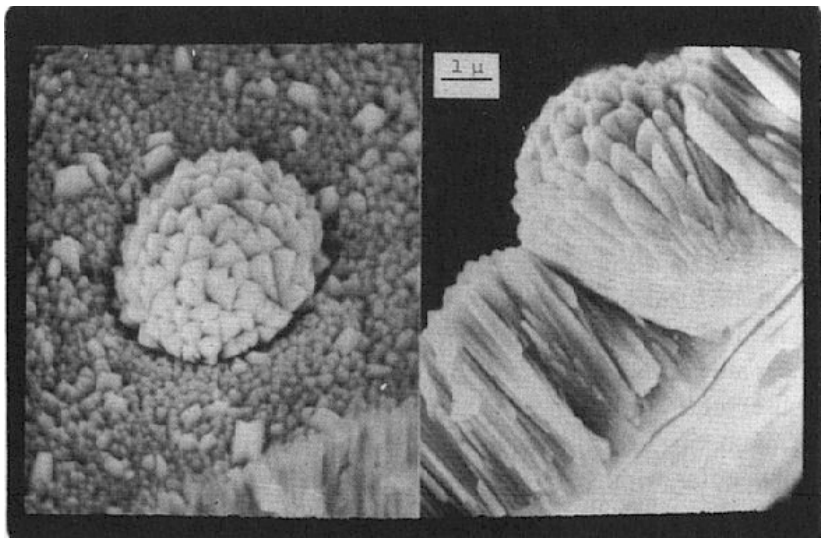


Figure 9-8. Nodule in sputter deposited chromium showing macrocolumnar morphology.

Surface Coverage

Surface coverage is the ability to cover the surface without leaving uncovered areas or pinholes. The surface coverage varies with the surface morphology, angle-of-incidence of the depositing material, nucleation

density and the amount of material deposited. In general, PVD processes have a poor ability to "close-over" a pinhole once it has formed as compared to electrodeposition and plasma deposition of amorphous materials.

The macroscopic and microscopic surface coverage of the deposited film on a substrate surface can be improved by the use of concurrent bombardment during film deposition (Sec. 8.2.4). The macroscopic ability to cover large complex geometries depends mostly on scattering of the depositing material in the gas phase.[178,179] On a more microscopic scale, sputtering and redeposition of the depositing film material will lead to better coverage on micron and submicron sized features[180]–[184] and reduce pinhole formation. On the atomic scale, the increased surface mobility, increased nucleation density and erosion/redeposition of the depositing adatoms will disrupt the columnar microstructure and eliminate the porosity along the columns.[185] As a result, the use of gas scattering, along with concurrent bombardment, increases the surface covering ability and decreases the microscopic and macroscopic porosity of the deposited film material as long as gas incorporation[186]–[188] does not generate voids.

Pinholes and Nodules

Pinholes are uncovered areas of the surface. They can be formed by geometrical shadowing during deposition or after deposition by the local loss of adhesion of a small area of material (pinhole flaking). Particulates on the surface present very local changes in surface morphology and local features develop such as the nodule shown in Fig. 9-8.[189]–[192] These features are poorly bonded to the film and often the pinholes in the film are not observable until the nodule is disturbed and falls out. For example, in a mirror coating, the film may not show many pinholes in the as-deposited state but after wiping or exposing the surface to ultrasonic cavitation, pinholes are developed. The resulting pinhole will be larger than the initiating particulate. This pinhole flaking from film deposited on surfaces and fixtures in the deposition system can be a major source of particulate contamination in the deposition system.

Nodules can also originate at any point in the film growth usually from particulates ("seeds") deposited on the surface of the growing film. This nodule formation process is particularly a problem when depositing multi-layer films such as anti-reflection optical coatings.[193] In depositing on a surface having a high-aspect-ratio via, such as shown in Fig. 9-1, the

corner at the bottom of the via is shadowed from deposition leaving a void sometimes called a "mouse hole."

9.4.3 Modification of Film Growth

The growth of the depositing film can be modified by a number of techniques.

Substrate Surface Morphology

The smoothness or roughness of the substrate surface has a pronounced effect on the film properties. If the substrate surface morphology is not controlled, then the film growth and properties can be expected to vary. Generally a film deposited on a smooth surface will have properties closer to the bulk properties than will a film deposited on a rough surface.

Angle-of-Incidence

The mean angle-of-incidence of the depositing atom flux will depend on the geometry of the system, the vaporization source, the fixturing and the fixture movement. These should be reproducible from run-to-run in order to deposit a reproducible film. Generally the more normal the angle-of-incidence of the depositing atom flux the higher the density of the film and the more near to bulk values for the materials properties that can be attained.

Modification of Nucleation during Growth

Reactive gases in the deposition system can influence the growth, structure, morphology and properties of the deposited films.[194-196] The origins of these effects are poorly understood but some portion of the effects can be attributed to changing the surface mobility of the adatom. In the sputter deposition of aluminum conductor materials for semiconductor devices, it has been shown that a small partial pressure of nitrogen during sputter deposition can have an effect on the electromigration properties of the deposited aluminum film. In the case of reactive deposition, the residual gas partial pressure is high and has a major effect on the surface

mobility and the development of columnar morphologies even at high deposition temperatures.

The periodic introduction of oxygen during aluminum deposition has been shown to suppress the development of the columnar growth morphology.[197][198] The same effect is seen for nitrogen on beryllium films.[199] A similar technique is used in electroplating where "brightening" is produced using additives to the electroplating bath that continuously "poison" the surface causing the film to continuously re-nucleate giving a smooth surface.

Energetic Particle Bombardment

In PVD processing, bombardment by energetic atomic-sized particles during growth can affect the film properties. This energetic film deposition process is called ion plating (Ch. 8) and the bombardment can have a variety of effects on film growth.[200] The bombardment can be continuous or periodic. Periodic bombardment can be every few angstroms, which will give an isotropic structure, or can be every hundreds or thousands of angstroms to give a multilayer structure. Energetic particles that bombard the growing film can arise from:

- High energy reflected neutrals during sputtering in low-pressure sputter deposition
- Ions accelerated to the surface from a plasma during ion plating with an applied or self-bias
- Ions accelerated away from an ion or plasma source in vacuum such as used in the IBAD processes

In some cases, such as bombardment by high energy reflected neutrals, the bombardment may be uncontrolled and un-appreciated. To have a controlled and reproducible process means that the energetic particle bombardment must be reproducible.

The momentum and energy exchange and the effects on a surface are discussed in Sec. 6.2.1. Bombardment effects are shown in Fig. 6-1, and include:

- Production of secondary electrons that are accelerated away from the cathode/substrate surface
- Reflection of some of the impinging high energy particles as high energy neutrals

- Generation of collision cascades in the near-surface region
- Physical sputtering of surface atoms
- Forward sputtering from some types of surface features
- Heating of the near-surface region
- Generation of lattice defects by recoil of atoms from their lattice position
- Trapping of the bombarding species at lattice defects
- "Stuffing" of atoms into the lattice by recoil processes which create compressive stresses
- Recoil implantation of surface species into the near-surface region
- Enhanced chemical reactivity on surface (bombardment-enhanced-chemical-reactivity)
- Backscattering of sputtered species if gas pressure is high (>20 mTorr)

In a growing film that is being concurrently bombarded by energetic particles, the surface and near-surface region is continually being buried and the bombardment effects are trapped in the growing film.[14][201]

Most of the bombarding energy is lost in the near-surface region in the form of heat. This heating can allow atomic motion such as diffusion and stress annealing, during the film formation process. If the thermal conductivity of the film is low, the surface region of the film can have an increasingly higher temperature as the film grows in thickness, especially if the thermal input into the surface is high. The amount of change depends not only on the temperature but the time-at-temperature. This means that the film properties can vary throughout the thickness of the film. In some cases, the temperature of the bulk of the material can be kept very low while the surface region is heated by the bombardment. This allows the development of a very high temperature gradient in the surface and near-surface regions.

Particle bombardment of the growing surface causes "atomic peening" where surface atoms are struck and recoil into voids and interstitial sites in the lattice of the surface region. This causes densification of the material[163] and introduces compressive stresses into the film. The densification changes a number of properties of the deposited film material. Bombardment typically reduces the grain size in the film but heating can

cause grain growth. Bombardment also causes sputtering and redeposition of the film material, which may be an important factor in densification.[185] Figure 9-9 shows the effect of concurrent bombardment on the morphology of sputter depositied chromuim films. Film A had no bombardment during deposition. The surface (top) is very rough and the fracture crossection (bottom) shows a very columnar morphology. With a 500 volt bias during deposition, Film B was densified and the surface was much smoother. The amount of bombardment is often measured by the amount of depositing material that is sputtered from the growing film[180] or the addition energy per depositing atom that is added to the surface.[202][203] The sputtering can cause removal of contaminants from the growing film.[204]

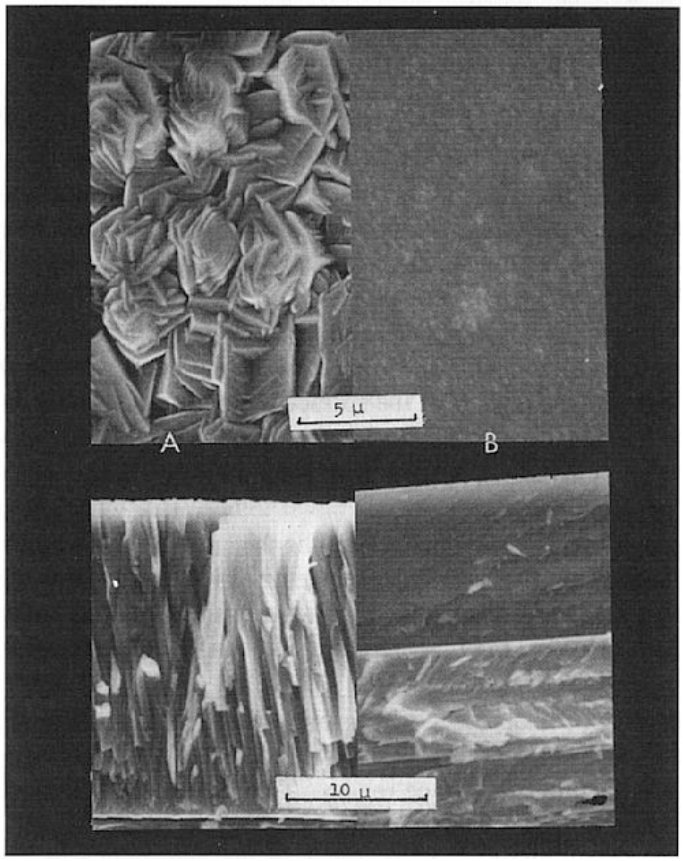


Figure 9-9. Surface (top) and fracture crossection (bottom) of sputter deposited chromium films with (*B*) and without (*A*) concurrent bombardment.

Mechanical Disruption

The development of the columnar morphology can be disrupted by mechanical means.[205] For example, the surface can be brushed or burnished periodically during the deposition to deform the surface.* Burnishing during deposition can also be used to reduce pinhole formation in the film.

9.4.4 Lattice Defects and Voids

Lattice defects are missing atoms (vacancies) or atom clusters, and lattice misalignments such as dislocations. Voids are internal pores that do not connect to a free surface of the material and thus do not contribute to the surface area but do affect film properties such as density. During film growth, vacancies are formed by the depositing atoms not filling all of the lattice positions. These vacancies can agglomerate into "microvoids" in the crystal structure.[206]–[209] Lattice defects in the films can be reduced by increased substrate heating during deposition or controlled concurrent ion bombardment during deposition.[210]

Lattice defects in the film can affect the electrical conductivity[211] and electromigration in metallic films and carrier mobility and lifetime in semiconductor materials. Generally high defect concentrations result in poor electromigration properties.[212] Lattice defects have been shown to be important to the properties of the high transition temperature superconductor films.[213]

In depositing a film under concurrent bombardment condition, the defect concentration is a function of the energy of the bombardment. The number of lattice defects initially decreases with bombarding energy, then increases above some value that is about 200 eV.[214][215]

The objective of the development program was to produce a thick aluminum film on the inside of a mild steel tube which could be anodized using a sulfuric acid anodizing bath. Any pinhole allowed rapid chemical attack of the mild steel. It was found necessary to burnish the aluminum several times during the deposition to close up pinholes and columnar morphology. A technique was developed that alternately moved the sputtering source and a burnishing brush (bottle-brush) along the axis of the rotating tube. This produced a pore-free coating that could be anodized.

9.4.5 Film Density

Film density is important in determining a number of film properties such as electrical resistivity, index of refraction, mechanical deformation, corrosion resistance, and chemical etch rate. Under non-bombardment conditions at low temperature, the morphology of the deposited film is determined by geometrical effects, with angle-of-incidence of the depositing particles being an important factor in the resulting film density. Under bombarding conditions, recoil implantation, forward sputtering, sputtering and redeposition, increased nucleation density, and increased surface mobilities of adatoms on the surface under bombardment conditions can be important in disrupting the columnar microstructure, and thereby increasing the film density and modifying film properties.[216][217] The energetic particle bombardment also improves the surface coverage and decreases the pinhole porosity in the deposited film. This increased density and better surface coverage is reflected in film properties such as: better corrosion resistance, lower chemical etch rate, higher hardness, lowered electrical resistivity of metal films, lowered gaseous and water vapor permeation through the film and increased index of refraction of dielectric films.[218]–[220]

9.4.6 Residual Film Stress

Invariably, atomistically deposited films have a residual stress which may be tensile or compressive in nature and can approach the yield or fracture strength of the materials involved. The exact origin of the film stress is not completely understood but can be visualized by using the model that tensile stress is due to the atoms becoming immobile (quenched) at spacings greater than they should be at the surface temperature. Compressive stresses are due to atoms being closer together than they should be, often due to atomic peening of film atoms but also possibly due to foreign interstitial or substitutional atoms in the lattice.[221] If there has been a phase change either due to reaction on the surface or during cool-down after deposition, the stress may be due to the volumetric change accompanying the phase change. In many cases, the stresses in a deposited film are anisotropic due to the angle-of-incidence distribution of the depositing atom flux and/or the bombarding ion flux.

Either compressive or tensile stresses can be introduced into the film due to differences in the thermal coefficient of expansion of the film

and substrate material if the deposition is done at elevated temperature. The differences in the coefficient of thermal expansion of the substrate and film material can produce thermal (shrinkage) stresses that put the film in tension or in compression depending on which material has the greater thermal expansion coefficient. Figure 9-10 shows a CVD TiC film which was deposited on POCO graphite at 1000°C and cooled to room temperature. The TiC shrank more than the graphite causing a tensile stress that cracked the coating. The figure also shows the columnar structure and nodules that can develop in CVD coatings when the partial pressure of the precursor vapor is too high.

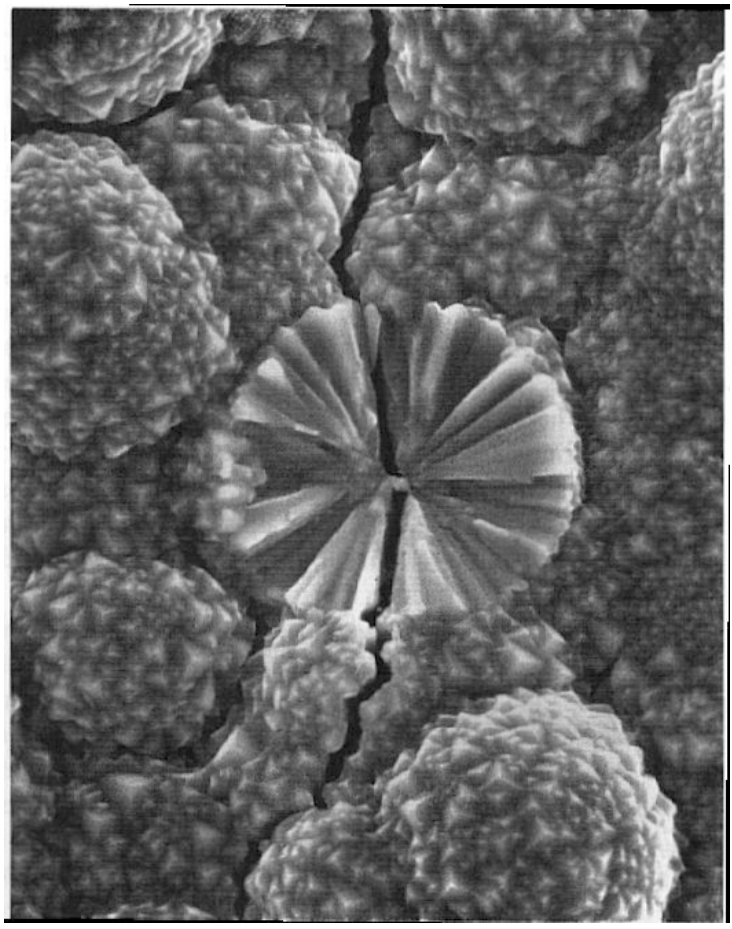


Figure 9-10. TiC deposited by chemical vapor deposition (CVD) on POCO graphite at a high temperature which cracked on cooling due to the differences in the thermal coefficient of expansions of the two materials.

Generally, vacuum deposited films and sputter-deposited films prepared at high pressures (>5 mTorr) have tensile stresses which can be anisotropic. In low pressure sputter deposition and ion plating, energetic particle bombardment can give rise to high compressive film stresses due to the recoil implantation of surface atoms.[222]-[226] Studies of vacuum evaporated films with concurrent bombardment have shown that the conversion of tensile stress to compressive stress is very dependent on the ratio of bombarding species to depositing species.

The residual film stress anisotropy can be very sensitive to geometry and gas pressure during sputter deposition. This is due to the anisotropic distribution of sputtered atom flux,[227] anisotropic bombardment by high energy reflected neutrals and the effect of gas-phase and surface collisions at higher pressures. Figure 9-11 shows the effect of gas pressure on residual film stress in post-cathode magnetron sputter deposition of molybdenum.[228][229] The figure shows anisotropy in film stress in two different axes of the film. There is a high compressive stress at low deposition pressures, high tensile stresses at higher pressures and low stress, due to a low density film at even higher pressures.

Films under compression will try to expand If the substrate is thin, the film will bow the substrate with the film being on the convex side. If the film has a tensile stress, the film will try to contract, bowing the substrate so the film is on the concave side. Tensile stress will relieve itself by microcracking the film. Compressive stress will relieve itself by buckling giving wrinkled spots (associated with contamination of the surface) or a wavy pattern (clean surface).[230] Compressive stress in a ductile material can relieve itself by generating “hillocks” (mounds of material). The stress distribution in a film may be anisotropic and may even be compressive in one direction and tensile in another.

The lattice strain associated with the residual film stress represents stored energy, and this energy together with a high concentration of lattice defects can lead to: (1) lowering of the recrystallization temperature in crystalline materials, (2) a lowered strain point in glassy materials, (3) a high chemical etch rate, (4) electromigration enhancement, (5) room temperature void growth in films (Sec. 9.6.6), and (6) other such mass transport effects.

The total film stress is the film stress times the thickness. In many applications, the total film stress should be minimized. For example, if a film with a high compressive stress is deposited on a glass surface, the glass will be under tensile stress which will decrease the strength of the

glass. There are several methods of modifying the mechanical stresses developed in films during growth. The techniques include:

- Limiting the thickness of the stressed film
- Concurrent energetic particle bombardment during deposition to maintain a zero stress condition
- Periodically alternating the concurrent bombardment conditions to form layers with alternatively tensile and compressive stresses that offset each other[228][229]
- Periodically adding alloying or reacting materials
- Mixing of materials[231]
- Deliberately generating an open columnar morphology that cannot transmit a stress

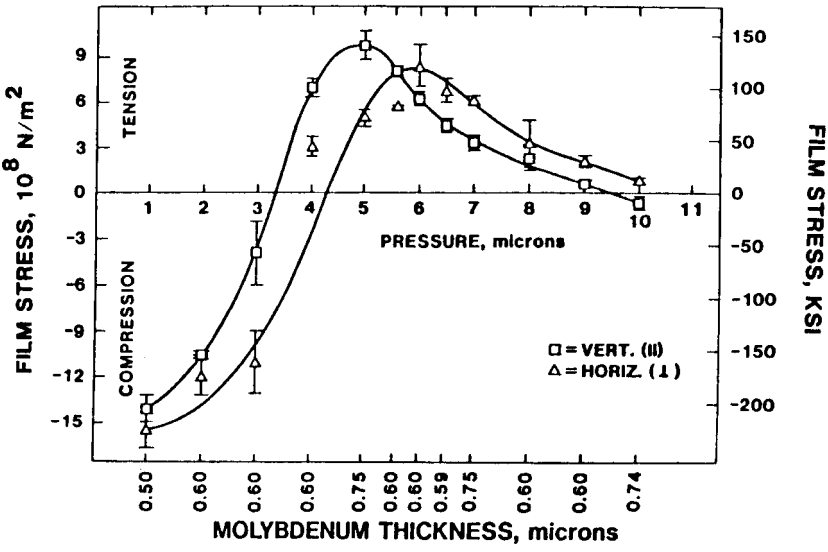


Figure 9-11. Effect of gas pressure on residual film stress in a post-cathode magnetron sputter deposited molybdenum film.[228]

Limiting the film thickness is generally the most easily accomplished approach. As a "rule-of-thumb" the thickness of high modulus materials such as chromium and tungsten should be limited to less than 500 Å to avoid excessive residual stress. If the film thickness is to exceed that value, some technique for stress monitoring and control should be developed.

One technique to control film stress is by using concurrent ion bombardment during deposition to create compressive stress to offset the tensile stress. By carefully controlling the bombardment parameters it is possible to find a zero stress condition.[232] Unfortunately, this condition is usually very dependent on the process parameters and the proper conditions are hard to control and maintain. A more flexible technique is to alternately deposit layers having tensile and compressive stresses that offset each other. This may be done by varying the concurrent bombardment from the reflected high energy neutrals in sputter deposition, by ions in ion plating, or from an ion gun.

9.4.7 Crystallographic Orientation

It is often found that a preferential crystallographic orientation or texture develops in deposited films.[233] This texturing can lead to non-isotropic film properties. The crystallographic orientation of the grains in the film is determined by the preferential growth of certain crystal planes over others.[156] This orientation may be altered by epitaxial growth on a substrate or by concurrent energetic ion bombardment.[234] Under bombardment condition, the more densely packed crystallographic planes are parallel to the direction of the impinging bombardment.

Epitaxial Film Growth

Epitaxy is defined as the oriented overgrowth of film material and typically refers to the growth of single crystal films.[235] Homoepitaxy is the epitaxial growth of a deposit on a substrate of the same material (e.g., doped Si on Si). Heteroepitaxy is the epitaxial growth of a deposit on a substrate of a different material (Au on Ag, GaAs on Si). Epitaxial growth requires some degree of mobility of the atoms and nuclei on the surface. An "epitaxial temperature" necessary for epitaxial growth in specific systems and under specific deposition conditions is sometimes specified.[39]

Single crystal overgrowth can be accomplished with large mismatches in lattice parameters between the film and substrate either by keeping the thickness of the deposited material small so that the mismatch can be taken up by straining the film lattice without forming lattice defects ("strained layer superlattice"), or by using a "buffer" layer to grade the strains from the substrate to the film. For example, thick single crystal SiC layers can be grown on silicon by CVD techniques even though the lattice mismatch is large (20%).[236] This is accomplished by forming a buffer layer by first carbonizing the silicon surface and then grading the composition from the substrate to the film. However, in general, if the lattice mismatch is large, the interface has a high density of dislocations and the resulting film will be polycrystalline.

Energetic adatoms and low energy ion bombardment during deposition can be used as a partial substitute for increased substrate temperature in epitaxial growth process. Carefully controlled bombardment can lower the temperature at which epitaxy can be obtained.[10][237] This is probably due to increased surface mobility of the adatoms. Ion beams of the depositing material ("film ions") have also been used to deposit epitaxial films.[238]

Oriented growth can be enhanced by "seeding" of the substrate surface with oriented nuclei. Such "seeds" can be formed by depositing a small amount of material, heating the surface to form isolated oriented grains and then using these grains as seeds for the deposition of an oriented film at a lower temperature.[239]

Amorphous Film Growth

Amorphous materials are those that have no detectable crystal structure. Amorphous film materials can be formed by:

- Deposition of a natural "glassy" material such as a glass composition[240][241]
- Deposition at low temperatures where the adatoms do not have enough mobility to form a crystalline structure (quenching)[101]
- Ion bombardment of high modulus materials during deposition[242]
- Deposition of materials some of whose bonds are partially saturated by hydrogen—examples include a-Si:H, a-C:H, and a-B:H.[81][82]

- Sputter deposition of complex metal alloys[243]
- Ion bombardment of films after deposition[244]

Metastable or Labile Materials

Metastable or labile phases are phases of materials that are easily changed if energy is available for mass transport processes to occur. Deposition processes can allow the development of metastable forms of the material. Metastable crystal structures can be formed by rapid quenching of high temperature phases of the deposited material or can be stabilized by residual stresses or impurities in the film. For example, diamond which is a metastable phase of carbon, is formed naturally in a high pressure and temperature environment, and changes to graphitic carbon on heating. However, diamond films can be deposited using the proper low-temperature vacuum deposition techniques (Sec. 9.7.8). Metastable film compositions can be formed under deposition conditions that do not allow precipitation of material when it is above the solubility limit of the system. For example, concurrent low energy ion bombardment using "dopant ions" allow doping of semiconductor films to a level greater than can be obtained by diffusion doping techniques.[245]

9.4.8 Gas Incorporation

Bombardment of a surface with gaseous ions during film growth or sputter cleaning can incorporate several atomic percent of gas in the near-surface region. Bombardment of the growing film by a gaseous species can result in the gas being incorporated into the bulk film since the surface is being continually buried under new film material. This effect is similar to the process of inert gas pumping in a sputter-ion pump. Very high concentrations of normally insoluble gases can be incorporated into the film structure.[246][247] For example, up to 40 at% hydrogen and helium can be incorporated into gold films. Using He^3 and NMR techniques it was shown that the helium is atomically dispersed but can be caused to agglomerate into voids on heating.[248]

To prevent gas incorporation in the surface or growing film, the surface can be heated to desorb the gases before they are covered over or the bombardment energy can be less that a few hundred eV which will

prevent the physical penetration of the ions into the surface. Typically a substrate temperature of 400°C or an ion energy of less than 250 eV will prevent the incorporation of argon ions into a film structure.

9.5 REACTIVE AND QUASI-REACTIVE DEPOSITION OF FILMS OF COMPOUND MATERIALS

Reactive deposition is the formation of a film of a compound either by co-deposition and reaction of the constituents, or by the reaction of a deposited species with the ambient gaseous or vapor environment. Reaction with a gaseous ambient is the most common technique. In the case of reactions with a gas or vapor if the reacting species form a volatile compound, etching results.[249][250] If the product of the reacting species is non-volatile, a compound film is formed.[251] Co-deposition of reactive species does not necessarily mean that they will chemically react to form a compound. For example, a mixture of Ti and C may not have any TiC; may be partially TiC and the rest an unreacted mixture of Ti and C; be substoichiometric TiC_{1-x}; or be TiC with excess Ti or C—all of which have different properties.

Generally, for the low temperature deposition of a compound film, one of the reacting species should be condensable and the other gaseous, e.g. Ti + N. If both are condensable, e.g. Ti + C, the best deposition condition is to have a high substrate temperature to promote reaction or use post-deposition heat treatment to react the mixture. The stoichiometry of a deposited compound can depend on the amount of reaction that occurs before the surface is buried. This depends on the amount of reactants available, the reaction probability, and the deposition rate. Reactively deposited films of oxides, carbides, nitrides, and carbonitrides are commonly used in the optics, electronics, decorative and mechanical applications.

In quasi-reactive deposition, the compound material is vaporized in a partial pressure of reactive gas that aids in replacing the species lost in the transport from the vaporization source to the substrate. Quasi-reactive deposition typically does not require as high a partial pressure of reactive gas as does reactive deposition since most of the reactive gas is supplied from the vaporizing source.

9.5.1 Chemical Reactions

Reaction with the gaseous ambient requires that the condensed species (e.g., Ti) react with the flux of a gaseous (e.g. nitrogen) incident on the surface. There are a number of techniques for performing reactive atomistic film deposition. The simplest way is to thermally evaporate the material in a partial pressure of a reactive gas in the process called reactive evaporation (Sec. 5.13.1). This generally produces a poor quality film because the materials are not completely reacted and the high gas pressures necessary for reaction result in gas phase collision and nucleation creating a low density deposit. Better quality films are obtained by promoting the chemical reaction by activating the reactive gas. Typically gaseous reactive species are in the molecular form, i.e., N_2, O_2, H_2, etc. The molecular species is less chemically reactive than the atomic species of the gas. An advantage of reaction with a gaseous species is that if the reaction does not occur, then the gas will generally leave the surface and not become entrapped in the film. Concurrent energetic particle bombardment can also be used to promote the chemical reaction.

Reaction can be with a co-depositing species either from a vaporization source or from a chemical vapor precursor such as acetylene (C_2H_2) for carbon. In this case, if the reaction does not occur, the depositing species are just mixed and the properties of the film will not be the same as if they had chemically reacted. The substrate temperature and concurrent bombardment conditions are very important in promoting chemical reactions on the surface. To obtain the proper and reproducible chemical composition of the film requires very careful control of the process. Use of chemical vapor precursors introduces problems with gas phase nucleation of very fine particles and the deposition of one film constituent (e.g. carbon) everywhere in the system. The formation and deposition of this material must be taken into consideration in designing the equipment and instrumentation, and when establishing a cleaning program for the deposition chamber and the pumping system.

Reaction Probability

The probability of chemical reaction between an impinging gas species and an atom in the surface depends on a number of factors including:

- Temperature of the surface
- Energy input into the surface
- Chemical reactivities of the incident and surface species
- Extent of prior reaction on the surface (i.e., whether the surface composition is $TiN_{0.1}$ or $TiN_{0.95}$)
- Relative fluxes of condensing species and incident gaseous species (i.e., the "availability" of the reactive species)
- Residence time (adsorption) of reactive species on the surface
- Radiation by electrons and/or photons capable of stimulating chemical reactions on the surface
- Kinetic energy of the incident reactive species
- Concurrent bombardment by energetic species not involved in the reaction (e.g., concurrent Ar ion bombardment during Ti + N deposition)

For an ambient pressure of 10^{-3} Torr, gaseous particles will impinge on a surface at about 10^3 monolayers per second compared to typical atomistic deposition rates of 10 or so monolayers per second. The impinging species may be reflected, with a short residence time, or may be adsorbed with an appreciable residence time.[252] Adsorbed species will be available for reaction for a longer period of time than the reflected species and may be mobile on the surface. The adsorption probability and adsorbed film thickness will depend on a number of factors such as the impinging species, nature of the surface, adsorption sites, etc. For instance, it has been shown that atomic oxygen on silicon will adsorb with a higher probability and to a greater thickness than molecular oxygen,[253] and that ozone (O_3) is strongly adsorbed on Al_2O_3 whereas O_2 is not.[254] It has also been shown that the surface stoichiometry affects the adsorption. For example, stoichiometric TiO_2 surfaces do not adsorb oxygen while substoichiometric surfaces absorb oxygen, with the amount depending on the stoichiometry. In plasma CVD of silicon from silane (SiH_4), it has been shown that the disilane species formed in a plasma has a higher adsorption probability than silane and the adsorption is important in the deposition of amorphous silicon at low temperatures.[81][82]

In deposition processes, the surface is continually being buried by new material. The probability that an adsorbed species will react with a surface depends on the nature of the species, the availability of the reactive

species, the degree of reaction that has already occurred at the surface and the time before burial. For example, oxygen molecules will react with a pure aluminum film but nitrogen molecules will not. The probability that the oxygen molecule will react with the aluminum decreases as the aluminum reacts with the oxygen molecules and the oxygen coverage increases. For example, in the case of atomic oxygen on silicon surfaces, the reaction probability will decrease monotonically with coverage through several monolayer coverages.[253] If the material can form a series of compounds (for example: TiN, Ti_2N) the probability of reaction is further decreased as the degree of reaction increases and it will be more difficult to form the higher compound (i.e., TiN will be more difficult to form than the Ti_2N). In many cases, surface reaction occurs first at active sites on a surface providing a non-homogeneous growth mode.[255][256] The extent to which this occurs in reactive film deposition is not known.

Free electrons can enhance chemical reactions in the vapor phase and on a surface. Electron energies of about 50 eV are the most desirable.[257] The effect of electrons on reactive deposition is relatively unknown. Photon radiation can enhance chemical reactions by exciting the reacting species (photoexcitation) thereby providing internal energy to aid in chemical reactions.[258–260]

Reactant Availability

The degree of reaction of co-depositing species depends on the availability of the reactive species.[152] Therefore the relative fluxes of the reactants is important. This gives rise to the "loading factor" which mean that there is a relationship between the surface area for reaction (deposited film area on substrates, fixtures and other vacuum surfaces) and the amount of reaction gas available.[153]

Many materials form a series of stable compounds that have different crystal structures. For example titanium and oxygen form: TiO, Ti_2O_3, TiO_2 (brookite), TiO_2 (anatase) and TiO_2 (rutile). By controlling the availability of the reactive gas and the deposition temperature, the composition and phase of the resulting film material can be controlled. This allows the gradation of composition from an elemental phase to the compound phase. For example, in the deposition of titanium nitride TiN, the deposition can be started with no nitrogen available so that pure titanium is deposited and then the nitrogen availability is increased so as to grade the composition to TiN. This technique of having a "graded interface"

or "buffer layer" between the substrate and the functional film, is often helpful in obtaining good adhesion of compound films to surfaces. Another example is the deposition of a nitride film on an oxide surface where the deposited material is graded through an oxide and oxy-nitride composition to the final nitride composition.

9.5.2 Plasma Activation

The gaseous reactive species may be "activated" to make them more chemically reactive and/or more readily adsorbed on surfaces and thus increase the reaction probability. The reactivity of the species can be increased by adding internal energy to form "excited species" or by fragmenting the species to form charged and uncharged "radicals," such as O, N or F, or $O^{+ \text{ or } -}$, N_2^+, N^+, or by forming a new gaseous reactive species such as ozone (O_3) from O_2 + O. Activation is most often done in a plasma. Such activation is done in reactive sputter deposition, reactive ion plating, Plasma Enhanced CVD (PECVD) and Activated Reactive Evaporation (ARE). Activation of the gaseous species can also be done using other means such as by radiation adsorption (e.g,. "photoexcitation" and "photodecomposition") from a source such as a mercury vapor lamp or an excimer laser, or "hot filament" decomposition of NH_4, F_2, and H_2.

A plasma produces a very complicated chemical environment which can produce reactive deposition processes that are not normally expected. For example, the sputter deposition of gold on oxide surfaces in an oxygen-containing plasma gives rise to very adherent gold films.[69]–[75] It has been shown that the deposition of gold in an oxygen plasma gives rise to Au-O bonding[70] and possibly the formation of some Au_2O_3.[75] This may be due to the formation of activated oxygen species in the plasma or the formation of a more readily adsorbed (e.g. O_3) reactive species.

9.5.3 Bombardment Effects on Chemical Reactions

Ions of reactive species can be produced in a plasma near the substrate surface or in a separate ion or plasma source, accelerated and used to bombard the depositing material.[261]–[264] For particle energies greater than a few hundreds of eV, the energetic particle will physically penetrate into the surface thereby increasing its "residence time." For example, it has been shown that for N_2^+ ions, having an energy of 500 eV

impinging on a depositing aluminum film, all of the nitrogen will react with the aluminum up to a N:Al deposition ratio of 1:1.[265] In addition, energetic particle bombardment will aid in chemical reactions.

The reactivity between co-deposited or adsorbed species can be increased by utilizing concurrent energetic particle bombardment by an inert species that does not enter into the reaction. Concurrent energetic inert particle bombardment during reactive film deposition has been shown to have a substantial effect on the composition, structure and properties of compound films. In general, the bombardment:

- Introduces heat into the surface
- Generates defects that can act as adsorption and reaction sites
- Dissociates adsorbed molecular species
- Produces secondary electrons which may assist chemical reactions
- Selectively desorbs or sputters unreacted or weakly bound species

This process has been termed "bombardment-enhanced-chemical-reaction."[266]–[270] It is of interest to note that Coburn and Winters attribute the major portion of bombardment-enhanced etching of silicon with fluorine to the development of the volatile higher fluoride (SiF_4) (i.e., more complete reaction) under bombardment conditions. Periodic bombardment of a depositing species by energetic reactive species can accomplish many of the same effects.[271] For example, an aluminum oxide film can be produced by depositing several monolayers of aluminum then bombarding with energetic oxygen ions followed by the deposition of more aluminum, etc. By doing this many times a compound film is deposited.[272]

9.5.4 Getter Pumping During Reactive Deposition

Getter pumping can be an important factor in mass flow control during reactive deposition where the depositing film material is reacting with the gaseous environment to form a film of a compound material. This in-chamber pumping reduces the partial pressure of the reactive gas during processing and changes the availability of the reactive gas. The amount of in-chamber pumping will depend on the area over which the film is being deposited. Thus it will make a difference as to how much deposition surface area is present ("loading factor"). Deposition rate will also be a factor.

9.5.5 Particulate Formation

In reactive deposition using a chemical vapor precursor such as C_2H_2, C_2H_4, or B_2H_6, plasma decomposition can allow the formation of ultrafine particles or "soot" (Sec. 5.12). This soot will assume a negative potential with respect to the plasma and not be deposited on surfaces which have a negative potential with respect to the plasma. However, when the plasma is extinguished, the soot will deposit on all surfaces in the chamber. To minimize the deposition of soot, the plasma can be extinguished by lowering the pressure while maintaining the plasma voltage and gas flow—this will help seep the soot into the pumping system.

Soot will accumulate on surfaces such as the screen on a turbopump inlet, turbopump stator blades and in mechanical pump oil. This necessitates periodic cleaning to remove the accumulations.

9.6 POST DEPOSITION PROCESSING AND CHANGES

After a film has been deposited it may be treated to further increase its functionality.

9.6.1 Topcoats

Porosity of the deposited films is often a limiting factor in their utilization. Various techniques can be used to fill the pores in the deposited film. For example, electrophoretic deposition of polymer particles has been used to selectively fill the pores in a dielectric film on a conductive substrate.[273] Topcoats can be used to protect the surface of coating from wear, abrasion, chemical attack, and environmental deterioration. For example, gold is used as a topcoat for many metallization systems in order to prevent corrosion and allow easy wire-bonding to the film surface. Polymer topcoat materials of acrylics, polyurethanes, epoxies, silicones, and siloxaines are available and are very similar to the coating materials that are used for conformal coatings and basecoats. These topcoats are used to improve abrasion and corrosion resistance of the film. In solvent-based formulations the nature and amount of the volatile solvent evolved is of concern in order to comply with environmental laws. "Solids content" is the portion of the coating formulation that will cure into a film, the

balance is called the "solvent content". The solids content can vary from 10–50 % depending on the material and application technique. Solvents can vary from water to various chlorinated solvents.

Coating materials can be applied by flowing techniques, such as flow (curtain) coating, dip coating, spray coating, spin coating or brush coating. The coating technique often determines the solids content of the coating material to be used. For example in flow coating, the solids content may be 20% while for dip coating the solids content may be 35% for the same coating material. Coatings are air-dried (to evaporate solvent) then cured by thermal or ultraviolet (UV) radiation. In thermal curing, the curing time and temperature can be determined by the substrate material. In the thermal curing process the resulting surface texture can be varied, which is useful for decorative coating. UV curing is desirable because the solvent content of the coating material can be reduced. The water-based urethanes can be dyed and are often used as topcoats on decorative coatings where the underlying metal film gives a high reflectance.

An important consideration in polymer coatings is their shrinkage on curing. For example, some UV-curing systems have shrinkages of 10–18% on curing. If the shrinkage is high, the coating thickness of the topcoat must be limited. In addition, the high coefficient of thermal expansion of many UV-curing systems limit their applications. UV-curing epoxy/acrylate resins have been developed that overcome these problems and allow curing of thick coatings (1 mil or greater) in a few seconds.

Acrylics are excellent for production coating because they are easy to apply, and can be water-based as well as chlorofluorocarbon (CFC) solvent-based. The evaporation-cured acrylic coatings can be easily removed by many chlorinated solvents. Polyurethane coatings are available in either single or two-component formulations as well as UV curing formulations. Moisture can play an important role in the curing of some polyurethane formulations. The water-based urethanes can be dyed and are often used as topcoats on decorative coatings where the underlying metal film gives a high reflectance. Epoxy coatings are very stable and can be obtained as two-component formulations or as UV curing single-part formulations. Silicone coatings are thermally cured and are especially useful for abrasion-resistant and chemical-resistant coatings and for high temperature applications (to 200°C). Polysiloxaine coatings are especially useful for abrasion-resistant topcoats for optical surfaces. Often a major concern in applying a topcoat is the presence of dust in the production environment. For optical applications, a Class 100 cleanroom may be

needed for applying the topcoat material to prevent pinholes and "fisheyes" in the coating which are then very obvious.

Plasma polymerization can be used to polymerize monomer materials into a polymer film.[274,275] A great deal of work is being done to integrate plasma polymerization into PVD processing.[276]–[280] This allows the film deposition processing and plasma polymerization topcoat processing to be done in the same equipment without having to open the system to the ambient.[281] Precursor vapor materials of interest which produce a siloxane coating by plasma polymerization are trimethylmethoxysilane (TMMOS), tetramethyldisloxane (TMDSO), hexamethyldisiloxane (HMDSO), and methyltrimethoxysilane (MTMOS). The mechanical and electrical properties of the siloxane coatings can be varied by controlling the degree of crosslinking and the degree of oxidation in the film.

9.6.2 Chemical and Electrochemical Treatments

After deposition, a film of a reactive material can react with gases and vapors in the ambient. For example, an aluminum film can react with oxygen to form a thin oxide layer which will increase in thickness with time or it can react with chlorine and corrode. If the film is less than fully-dense, there can be a large surface area available for reaction and the film properties can change significantly with time after the film has been exposed to the ambient. The large surface area can also adsorb and desorb gases and vapors and the amount can vary with the availability of the species. This effect is used in many thin film sensor devices. Deposited aluminum films can be electrolytically anodized[282][283] to form a dielectric coating layer. Chromate and phosphate conversion treatments are wet chemical surface treatments that are used to change the surface chemistry of metals to give corrosion resistance and bondability to paints, etc.[284]

Chromate conversion coatings are produced on various metals (Al, Cd, Cu, Mg, Ag, Zn) by chemical treatment (sometimes electrochemical) with hexavalent chromium solutions with "activators"(acetate formate, sulfate, chloride, fluoride, nitrate, phosphate and sulfamate ions) in acid solutions.[285] Application may be by immersion, spraying, brushing etc. This treatment creates a thin surface layer of hydrated metal-chromium compounds. These hydrated layers which initially are gelatinous and can be dyed, harden with age. The treatment provides corrosion protection by itself or changes a normally alkaline metal surface to an

acidic surface suitable for painting (alkaline surfaces saponify paints giving poor adhesion). Heating above 150°C can result in dehydration of the chromate layer and loss of protective qualities. Chromate coatings have some electrical conductivity and can be used on electrical contacts where corrosion products may, with time, degrade the electrical contacts—thin coatings are best for this purpose.

Phosphate conversion coatings are electrically non-conductive and are used to prepare surfaces (steel, Zn, Al) for painting, plastic coating, rubber coating, lubricants, waxes, oils, etc.[286] Phosphating solutions consist of metal phosphates in phosphoric acid. Upon immersion, the metal surface is dissolved and a metal phosphate is precipitated on the surface. "Accelerators" (nitrates, nitrites, chlorates, peroxides) are used to speed up the reaction and other reagents are used to decrease the polarization caused by hydrogen evolution. The phosphated surface is rinsed in weak chromic acid to remove the unreacted phosphating compounds. The phosphated surface is microscopically rough and provides a good mechanical bond to applied coating material or for waxes or oils if the coating is to be used by itself for corrosion protection (zinc phosphate).

9.6.3 Mechanical Treatments

Mechanical deformation can be used to densify films and cover pores in deposited thin films. Shot peening has been used to densify the M(etal)-Cr-Al films deposited on turbine blades to increase their hot-corrosion resistance.[287] Shot peening of aluminum coatings is used to densify the deposits.[284]

Burnishing is the mechanical deformation of a soft surface by brushing using a solid surface such as a cloth or by tumbling or agitation in a "pack" of hard particles. Soft metallic films can be burnished to reduce porosity.[288] In the deposition of pinhole-free films, it has been found that burnishing between several sequentially deposited layers can produce pinhole-free films. For example, by burnishing each layer of a 3-layer aluminum film, sputter deposited on mild steel, a film was obtained which could be sulfuric-acid anodized without attacking the steel substrate. This burnishing can be done in the PVD deposition system with the proper fixturing. Burnishing has the disadvantage that it is difficult to specify in production. Specifications typically have to be made on the behavior of the surface after burnishing.

9.6.4 Thermal Treatments

Post-deposition heating of films can be done in a furnace, by flash lamp heating such as used in Rapid Thermal Processing (RTP) techniques[289]–[292] or by laser irradiation.[293] Post-deposition heating can create film stresses due to differences in the coefficient of thermal expansion between the film and substrate and between different phases in the film. These stresses can result in plastic deformation of the film or substrate material,[294] create stress-related changes in the film properties, or create interfacial fractures.*

Heating is used to promote mass transport (diffusion) so as to anneal the residual stress and defect structure in deposited films. For example, it has been shown that glass films exhibit strain points far lower than those of the bulk materials,[295] that grain growth can take place in sputter-deposited copper films at very low temperature,[296] and that stress relief in TiB_2 films occurs far below the annealing temperature of the bulk material.[297] Post-deposition heating has been shown to modify the structure and electrical properties of deposited SiO_2 films.[296] These effects are probably due to the residual film stress and high defect concentrations in the deposited films. Post-deposition heat treatments can be used to induce grain growth or phase changes but care must be taken in that the changes can result in increased film stress or fracture. The substrate material and structure can influence the kinetics of the phase change by influencing the nucleation of the new phase.[299] Post-deposition heating rarely allows densification of columnar films because the surfaces of the columnar structure react with the ambient and the surface layer that is formed prevents the diffusion needed for densification.

Post-deposition heating of some metal films can cause the film structure to agglomerate into islands generating porosity and changing the

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*Tungsten metallization: in fabricating the product, glass was metallized with tungsten. Adhesion tests showed that the adhesion was good. The product was then heated to 500 °C and the adhesion was still good. On dicing by wet sawing, the film fell off. The problem was that the thermal cycling caused interfacial flaws to form because of the difference in coefficient of expansion of the glass and the tungsten. These flaws did not propagate until the moisture and vibration from sawing caused failure. The solution was to reduce the thickness of the tungsten so there would not be as much stress during thermal cycling.

optical and electrical properties of the films.[300]–[302] Agglomeration also occurs by grain boundary grooving of the film material.[303][304]

Post-deposition heat treatments are used to promote reaction between un-reacted co-deposited materials and to promote reaction of the deposited material with an ambient gas. For instance, it is common practice to heat deposited high temperature oxide superconductor films in an oxygen atmosphere to improve their performance. Indium-tin-oxide (ITO) films are heated in forming gas to increase their electrical conductivity.[305] Heating can also cause the formation of internal dispersed phases between co-deposited materials to produce dispersion strengthening.

Heating is used to alloy the deposited material with the substrate surface. Post-deposition diffusion and reaction can form a more extensive interfacial region and induce compound formation in semiconductor metallization (Fig. 9-3).[306][307] Post-deposition heating and diffusion can be used to completely convert the deposited material to interfacial material. For example, a platinum film on silicon can be heated to form a platinum silicide layer. The diffusion at the interface can be studied by the motion of "markers."[308][309] Post-deposition interdiffusion can result in the failure of a metallized semiconductor device by diffusion and shorting of the junctions.[310] Diffusion can be limited by using diffusion barriers. The XeCl (308 nm) excimer laser has been used to melt and planarize thin films of gold, copper and aluminum on silicon devices with submicron features.[311] Heating plus isostatic pressure is used to remove voids in semiconductor metallization.[312]

9.6.5 Ion Bombardment

Post-deposition ion bombardment using high-energy (1-10 MeV) reactive or non-reactive ions can be used to change the composition or properties[313][314] of the film material or to increase the interfacial adhesion by interfacial mixing or "stitching."[315]–[319]

To "recoil mix" or "stitch" an interface, the films must be rather thin (<1000Å) and the ion energies are selected to give the peak range just beyond the interface. In recoil mixing at an interface, if the materials involved are miscible, the ion mixing results in interfacial reaction and diffusion. However if the materials are not miscible, the interfacial region is not mixed but the adhesion is increased. Generally there is a dose dependence on adhesion improvement with the best result being for doses of 10^{15}–10^{17} ions per cm^2 while excessive bombardment induces

interfacial voids. Part of the observed increase in adhesion may be due to the elimination of interfacial voids by "forward sputtering." Ion bombardment can also be used to anneal the film.[314] Most recently, the Plasma Immersion Ion Implantation (PSII) process (Sec. 2.6.2) has been used to treat deposited films, particularly hard coatings.

9.6.6 Post-Deposition Changes

High surface areas and high residual film stress are major factors in the change of film properties with time. The high surface area allows corrosion and adsorption to play major roles in the stability of film properties. Residual stress represents stored energy and can create long-term stability problems.

Adhesion (See Ch. 11)

In some cases film adhesion may increase or decrease with time under ambient conditions.[320][321] The increase in adhesion may be due to diffusion of reactive species to the interface or the relief of residual stresses. The film adhesion may decrease with time and may be due to static fatigue fracture at the interface due to residual stress and promoted by the presence of moisture or to corrosion of the interface by ambient or entrapped species.

Microstructure

High residual stress and high point defect concentrations can lead to time-dependent changes in the microstructure of the deposited material. For example, under some deposition conditions, sputter deposited copper films shows grain growth and recrystallization at room temperature.[296]

Void Formation

Voids are internal cavities in the film that may or may not contain a gaseous species. Voids are often spherical in shape to minimize their surface area. Often the voids are concentrated along grain boundaries, around precipitated phases, and/or at the interface between the film and the

substrate. Voids can be formed by several mechanisms. When atomistically depositing a film, there are generally a large number of point defects in the lattice structure. These defects can migrate to free surfaces or agglomerate into voids, particularly when the film is exposed to a high temperature. In multilayer film structures, the porosity in the film layers that are encapsulated can collapse into voids. The less dense the deposited film is, the more likely is the formation of appreciable number of voids.

If the deposited film has a high residual stress the stress can be relieved with time by the formation of voids (stress voids) even at room temperature.[322]–[327] If the film is encapsulated, then the voids will precipitate along grain boundaries and at interfaces. For example, in silicon technology, aluminum films are often deposited for electrical interconnects. The aluminum is patterned into long thin lines (connector stripes) having widths of less than a few microns. The aluminum conductors are then encapsulated in a dielectric material, using CVD technology, with a deposition temperature greater than 450°C. The as-deposited aluminum is very fine-grained but during the CVD process the aluminum grains grow to microns in size. On cool-down, the aluminum shrinks more than the encapsulating material putting the aluminum into tensile stress. At room temperature, over a period of time, this stress is relieved by forming voids which accumulate along the grain boundaries and can cause an electrical open in the connector stripe.* To avoid this problem, an Al: 2%Cu (Al[Cu]) or Al:2%Cu:1% Si (Al[CuSi]) aluminum alloy is used for the conductor. On heating particles of the intermetallic, Al_2Cu, are precipitated in

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*A semiconductor device production group had received word that some of their aluminum metallization lines were losing their conductivity ("opening-up") after several years in storage. The processing involved deposition of an aluminum metallization, defining the conductor path and then encapsulating the conductor line by CVD of a PSG film at 450 ^{0}C. The grain size of the film, after the high temperature CVD processing, was about the same as the conductor line width and failure was due to opening of the grain boundaries which extended across the conductor. They thought there had been a processing problem and were intensely reviewing the old process sheets. I proposed that the failure was due to grain growth during the CVD process and shrinkage stresses due to the difference of coefficient of expansion of the aluminum which is high and the silicon/PSG which was lower. I used the analogy to casting aluminum in a glass tube where, on cool down, the aluminum will shrink at the free surface leaving a shrinkage core in the center of the tube of aluminum. A casting engineer knows to allow for this shrinkage in his mold design. (Cont. pg. 503)

the aluminum grains and provides more surfaces on which the voids will form thus reducing the chance of creating an open conductor with time.[328][329] Encapsulation produces different effects on the mechanical properties of Al(Cu) and Al(CuSi) aluminum alloy films.[330] The presence of the Al_2Cu nuclei in an aluminum matrix forms a galvanic corrosion couple and corrosion pitting can occur if there is an electrolyte, such as a photoresist, present.

Electrical Resistivity

The electrical resistivity of the film can change after deposition due to progressive oxidation of the exposed surfaces. For example, if the film has a columnar morphology, the surfaces of the columns can oxidize and expand to come into better contact than before oxidation. The electrical path through the film then consists of metallic conductors in series with an oxide having a tunneling mechanism for electrical conduction. Since the temperature dependence of their coefficient of resistivity (TCR) are opposite, this structure can be constructed to have a net TCR of zero (i.e., the resistance is independent of temperature).

Electromigration

In electromigration, a high current density (in aluminum: 10^6 amps/cm^2—steady, 10^7 amps/cm^2—pulse) causes the movement of atoms and the loss of material in some regions (opens) and the accumulation

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(Cont. from pg. 502) In the CVD encapsulation there was no free surfaces so the aluminum, which undergoes grain growth during the CVD processing, was under a high tensile stress when cooled. Over a period of time the tensile stress created voids which agglomerate on surfaces such as the grain boundaries, giving an "open" in some cases. A survey of the literature showed that the problem had been recognized several years before and that the solution was to add copper to the aluminum metallization so that Cu-Al particles would form in the aluminum grains during the high temperature processing and act as nucleation sites for the voids thus distributing the voids throughout the grain and not just at the grain boundaries.

Note: This is an interesting problem since if you try to accelerate failure by heating, which is a common way of accelerating many failure processes, you decrease the driving force for failure, namely the tensile stress in the film—perhaps there would never be any failure under "accelerated aging" tests (Sec. 11.5.4).

(hillocks) of material in other regions.[331,332] The formation of voids, hillocks and electrical "opens" by electromigration is an important effect in semiconductor metallization where the current densities are high. Electromigration failure is very sensitive to the deposition process, the point defect concentration in the film material, and the processing environment. Electromigration is a statistical problem, with some failures occurring far below the mean value. Time-to-first-failure statistics are used rather than mean-time-to-failure statistics. Conductors which are susceptible to this failure are removed during the "burn-in" process where the conductors carry a current for a period of time before they are marketed. Electromigration can be minimized and the statistical spread can be lessened by process control, addition of dispersed particles (1% Si in Al), multilayering of the metallization (ex. 3000 Å aluminum alternated with 50-100 Å titanium), or the use of "cap" (passivating) material. The use of a silicon additive makes a sputter-deposited Al:2%Cu:1% Si alloy a common metallization material in silicon device technology. Figure 9-12 shows a typical "bathtub" curve for electromigration failure as a function of time for a typical "good" batch of aluminum metallization. Copper metallization is less prone to electromigration failure than is aluminum.

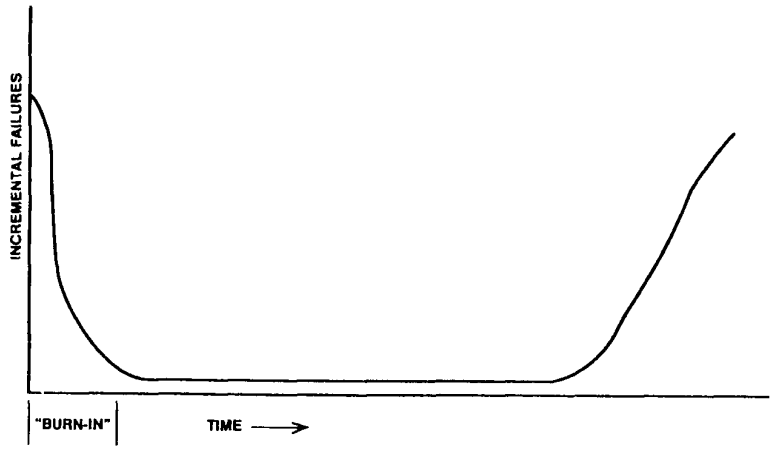


Figure 9-12. Electromigration failures as a function of time ("bathtub curve").

9.7 DEPOSITION OF UNIQUE MATERIALS AND STRUCTURES

9.7.1 Metallization

Metallic electrical conductor films are widely used in the hybrid microelectonics and semiconductor industry where thin film "blanket metallization," which covers the whole surface, is chemically etched or plasma etched into conductor patterns. The thin film material can also be deposited through a physical mask to form a conductor pattern on the surface. Masking techniques are useful on conductor geometries down to about 2–5 microns in width and have the advantage that they do not have to be chemically etched.

Table 9-3 gives the bulk resistivity of a number of metals used as electrical conductors. Gold has the advantage that it does not oxidize and therefore wires can easily bonded to the gold surface by soldering, thermocompression bonding, or ultrasonic bonding. It has the disadvantage that it does not adhere well to oxide surfaces. Silver is easily corroded and does strange things in the presence of moisture and is not often used as a metallization material. Copper is a very desirable thin film conductor material though it does not bond well to oxide surfaces when deposited by PVD techniques. Aluminum, deposited by PVD techniques, adheres strongly to oxide surfaces. Tungsten and the tungsten:10% titanium alloy are used in silicon technology as a diffusion barrier between the silicon and metallizations such as aluminum. The diffusion barrier prevents the aluminum from diffusing into the silicon during deposition and in subsequent high temperature processing. Conductive compounds such as TiN are also used as diffusion barrier materials.

Many metallization systems are multilayered to combine desirable properties. For example, in metallizing an oxide surface or a surface having an oxide surface layer, the first material to be deposited is an oxygen-active material such as chromium or Nichrome™ (60Ni:24Fe:16Cr:1C) or titanium to act as a "glue layer".[333] Before the chromium or titanium can oxidize, copper or gold, which are soluble in chromium, nickel and titanium, are deposited as the electrical conducting layer. When depositing copper, a thin gold topcoat film may be deposited to form a oxidation-resistant surface.

Titanium and gold in contact, form a galvanic corrosion couple. In the presence of an electrolyte, such as in wet chemical etching or if there is

trapped ionic material in the films, interfacial corrosion can occur giving a loss of adhesion. To disrupt this galvanic corrosion couple, a layer of platinum or palladium can be deposited between the titanium and the gold.[334]–[336] Thus a metallization system might be:

Ti (500 Å) - Pd (1000Å) - Cu (>10,000Å) - Au (500Å)

Table 9-3. Resistivities of Some Bulk Materials

Material	Bulk Resistivity (20°C, ohm-cm)
Silver	1.6×10^{-6}
Copper	1.7×10^{-6}
Gold	2.4×10^{-6}
Aluminum	2.8×10^{-6}
Tungsten	5.5×10^{-6}
Titanium	$\approx 50 \times 10^{-6}$

All of these materials can be easily thermally evaporated. The thickness of high elastic modulus materials such as Ti and Cr should be limited to less than 500Å in order to limit the total residual film stress. Nichrome™ is often used instead of chromium because of its lower elastic modulus. When Nichrome™ is thermally evaporated, the depositing film is initially chromium-rich and becomes nickel-rich as the deposition proceeds.

To avoid complex metallization systems, aluminum metallization may be preferable. When using aluminum metallization that is going to be encapsulated, stress voiding (Sec. 9.6.6) should be considered. Aluminum metallization is easily etched either using wet-chemical etching or a BCl_3 plasma.

One limiting factor in the use of PVD metallic films is the poor ability of the PVD techniques to fill high aspect ratio (narrow and deep) holes (vias) which are used to connect various levels in a semiconductor device. Chemical Vapor Deposition (CVD) techniques have a better ability to fill the holes with a high density metallization and tungsten CVD is often used for this purpose. Collimination techniques (Sec. 6.4.3) can be used to increase the ability of PVD processing to fill surface features.

9.7.2 Transparent Electrical Conductors

The resistivity of a thin film is often measured in units of ohms per square (Ω/□) (Sec. 10.5.7). Optically transparent electrical conductors are used as anti-static coatings (>1000 Ω/□), transparent resistive heaters (<10 Ω/□) and are a necessity for the electrodes (<100 Ω/□) of many types of optically-active thin film devices such as flat panel displays and electrochromic devices. There are several optically transparent semiconducting oxide materials that have lattice-defect-related (anion deficient) electrical conductivity.[337] These include indium oxide (In_2O_3) and tin oxide (SnO_2). The most commonly used transparent thin film material is an alloy of 90 wt%In_2O_3 and 10 wt%SnO_2 (indium-tin-oxide or ITO). The transparent conductor material is commercially deposited on glass, and polymers such as glass and molded polycarbonate windows and PET, OPP and PTFE webs.

ITO can be deposited by reactive deposition in oxygen from a mixed-metal (In:Sn) sputtering target or by non-reactive or quasi-reactive sputter deposition from a mixed-oxide target (tin oxide has a solubility limit of 10 wt% in indium oxide). The deposited film may be annealed after deposition in an oxygen, hydrogen or forming gas (90%N_2:10%H_2) atmosphere to increase the density and electrical conductivity. Ion bombardment during deposition (IBAD process) can increase the weatherability of thin ITO films. The properties of the ITO films depend strongly on the deposition technique, deposition parameters, the properties of the sputtering target, and post-deposition treatment.[337][338] Typically, reactively deposited ITO has a higher density and higher index of refraction than does non-reactively deposited material. With antireflection (AR) coatings, the visible transmission can be greater than 90% for sputtered deposited ITO films 1500 Å thick.

In many applications, large area substrates must be coated with a high degree of uniformity. This is often easier to accomplish using quasi-reactive sputtering of oxide targets than with reactive sputtering where the uniformity of the reactive gas distribution can be a problem. In some applications, pinholes are a major concern and this means that the cleanliness of the deposition system is important. Some fabricators maintain that less-than-fully dense oxide sputtering targets produce fewer particulates in the deposition system than do fully dense oxide targets. When sputtering either the mixed-oxide or mixed metal target, high-resistivity nodules form on the target surface. These nodules reduce the sputtering yield of the

target and must be periodically removed mechanically, which is a problem in high-volume production. The origin of these nodules is poorly understood.

Other electrically conductive transparent oxides include:[339] fluorine and chlorine doped oxides such as tin oxide (SnO_2 : Fl); antimony doped tin oxide (SnO_2:Sb); cadmium oxide (CdO); Cd_2SnO_4 and aluminum doped zinc oxide (ZnO:Al or ZAO). Non-transparent electrically conductive oxides include: chromium oxide (Cr_2O_3); the copper oxides (CuO, Cu_2O); lead oxide (PbO); and rubidium oxide (RbO) . In addition to sputter deposition, conductive oxide films can also be prepared by spray pyrolysis, reactive evaporation, and chemical vapor deposition.

9.7.3 Low Emissivity (Low-E) Coatings

Low emissivity (low-E) coatings reflect infrared (heat) and are used to retain heat normally lost through a window.[340] The coating is generally comprised of several thin film layers with a thin film of silver giving the thermal reflectance. The coating can be deposited on an interior glass surface of a double glazed window or on a web mounted between the panes of glass. Typically the low-E coating will reflect 85–95% of the thermal radiation back into the room while still giving a high (60–65%) optical transmittance. The thermal reflectance and the solar transmittance (shading factor) can be tailored to the local conditions. Typical basic low-E coatings are:

Glass:ZnO_x:Ag:Zn (thin):ZnO_x:TiO_x:Air
or
Glass:SnO_x:Ag:NiCr (thin):SnO_x:Air

Where x is less than 2 (i.e., substoichiometric ZnO_2 or SnO_2)

The first ZnO_x or SnO_x film acts as a nucleating surface for the depositing silver to give a high nucleation density, the Zn or NiCr protects the silver from oxidation during the deposition of the second ZnO_x or SnO_x film which serves to stabilize the silver surface and to decrease the optical reflectance of the silver film. A protective topcoat may or may not be used.

9.7.4 Permeation and Diffusion Barrier Layers

Barrier layers are used to prevent diffusion or permeation through to the underlying material (Sec. 10.5.9). A common permeation barrier layer material is aluminum film on polymers to slow the permeation of water vapor and gases through a flexible packaging material. The material is deposited in a web-coating machine. The aluminum has the disadvantage that it shields the contents from microwave heating. At present, a great deal of effort is being directed to developing a dielectric permeation barrier film since this would allow microwave heating of the contents of the package.[341]

In the semiconductor industry, diffusion barrier layers are used in metallization systems to prevent the diffusion and reaction of the deposited metallization material with the silicon in subsequent high temperature processing.[118][342] For example, in aluminum metallization tungsten, W-Ti[119] or titanium is used as the barrier film and in CVD-tungsten, Ti + TiN is used as the barrier layer.[343] The TiN prevents the high-temperature WF_6 CVD-precursor vapor from reacting with the titanium. If there are pinholes in the TiN the reaction will form "volcanoes" in the tungsten metallization.[312]

9.7.5 Porous Films

In some applications, porous films are desirable. For example, when a porous film is used as an electrode on an ionic material in an electrolyte, the ions that are released from the ionic material can easily pass through the electrode into the electrolyte.[344] High surface areas are often also desirable when the film is used as a catalytic or sensor material. Very porous film structures can be generated by having a rough substrate surface and/or by having a very oblique deposition flux which exacerbates the columnar growth morphology.

9.7.6 Composite (Two Phase) Films

Composite materials are materials that consist of phases of dissimilar materials either in the form of layers or phases dispersed in a matrix. In many applications, multi-layer film structures (layered composites) are used. Multilayer films having differing optical properties are used

in forming antireflecting coatings, heat mirrors, and band-pass filters on optical components. Multilayer thin films have many applications. The layers may be of different metals or may be a mixture of metals, oxides and polymers. For example, a multilayer structure of polymer and oxide has been shown to have excellent moisture and oxygen permeation barrier properties.[345]

Multi-layer composites of many alternating layers of materials having different fracture properties are use in wear-resistant applications. For example, 25 or so alternating thin layers of TiN and gold are used for decorative wear-resistant coatings on writing pen housings. As the gold wears it exposes TiN which has a gold color and is wear resistant—the pens are advertised as "gold plated." Many alternating layers of TiC_xN_y with different carbon and nitrogen compositions are used as tool coatings to improve fracture toughness of the coating. Alternating layers of TiN and NbN are also being investigated for tool coatings.[346]

Dispersed phase composite films can be formed by co-depositing insoluble materials. If the temperature is high enough for mass transport, the phases will separate giving a two-phase material. Composite materials can also be formed by co-depositing materials where the phase formed by reaction is dispersed in a matrix of the unreacted material.[347][348] For example, a reactive material such as titanium can be co-deposited with a less reactive material such as nickel in a reactive environment of oxygen or carbon to give dispersed phases of oxides (TiO_2) or carbides (TiC) in nickel. Composite films can be formed by a minor constituent reacting with the major constituent to form an intermetallic phase which is dispersed in the major phase. For example, in Al:2%Cu metallization, the Al_2Cu will precipitate to form a dispersion in the aluminum. This precipitate phase then acts as segregation sites for voids formed due to film stress. In cases where two or more materials are depositing at the same time on nonreactive surfaces, there may be changes in composition in the early stages of nucleation due to differing adsorption energies.[349]

The presence of second phase materials in a film may lead to galvanic corrosion problems when an electrolyte is present.[328][329] For example, Al-Cu films where the intermetallic phases Al_2Cu has precipitated, have been found to be more susceptible to intergranular and pitting corrosion than pure aluminum films.[350] The Al_2Cu acts as a cathode (-0.73 volts) while the Al acts as the anode (-0.85 volts). The corrosion effects become more important with increasing copper concentration so the copper in Al-Cu metallization is limited to 2–4% when a homogeneous distribution of the Al-Cu particles is desirable.[351]

Composite materials of metal particles in a polymer matrix can be formed by deposition of the metallic phase during plasma polymerization. Such a composite film has been shown to have a better wear durability than the polymer film alone[352] and to have interesting optical properties.[353]

9.7.7 Intermetallic Films

Intermetallic compounds are formed from electropositive and electronegative metals which chemically bond to form compounds with a specific composition and crystalline structure. Intermetallic films are often formed by depositing the film material on a hot surface so that the adatoms diffuse and react with the surface material converting it into a silicide, aluminide, etc. Very corrosion resistant intermetallic films can be formed by co-deposition processes at high temperatures. These include the very chemically-stable compounds Mo_5Ru_3 and W_3Ru_2[354] and $ZrPt_3$ and $ZrIr_3$ which are d-orbital bonded intermetallic compounds.[355]–[357]

9.7.8 Diamond and Diamond-Like Carbon (DLC) Films

Recently great progress has been made in the deposition of diamond and diamond-like carbon (DLC) coatings for industrial applications.[358] Natural diamond with its high hardness, low coefficient of friction, high thermal conductivity, good visible and infrared transparency, and chemical inertness has long provided a goal for the thin film deposition community.

Diamond is a carbon material with a specific crystallographic structure (diamond structure) and specific chemical bonding (sp^3 bonding). Diamond-like carbon (DLC) is an amorphous carbon material with mostly sp^3 bonding that exhibits many of the desirable properties of the diamond material. The DLC material is sometimes called "amorphous diamond"—an oxymoron that should be avoided.

The property of the carbon sp^3 bonding that allows the deposition of both diamond and DLC coatings, is its relative chemical inertness to hydrogen reduction. If the sp^3 bond is formed during deposition, then the carbon film is stable to hydrogen etching. If, however, the sp^2 (graphite) bond is formed, the material is much more susceptible to hydrogen etching.

Polycrystalline diamond films are formed if the deposition temperature is high enough (>600°C) to allow atomic rearrangement during deposition. DLC films are formed at lower temperatures (room temperature and even below) where the atoms cannot arrange themselves into the diamond structure giving an amorphous material. The DLC films can have varying amounts of sp^2 bonding and included hydrogen, which affect their properties. The sp^3-bonded material can be deposited by a number of techniques most of which involve "activating" both a hydrocarbon species, such as methane, to allow carbon deposition, and hydrogen to provide the etchant species.

Polycrystalline diamond films are most often deposited by a hot filament technique using a chemical vapor precursor (HFCVD), a combustion flame technique, or a Plasma Enhanced CVD (PECVD) technique using an rf (13.56 MHz) or microwave (2.45 GHz) plasma. In the hot filament process, the hot surface dissociates the gases, while in the flame process, the gases are dissociated in a reducing (hydrogen-rich) flame. In the plasma process, the gases are dissociated and ionized in the plasma. In all cases, the diamond film that is formed is polycrystalline and has a rough surface. This is due to the method of film nucleation on the substrate surface and the nature of the film growth. The rough surface has a high coefficient of friction and a great deal of development work is being done to try to improve the surface smoothness for wear and friction applications. The physical and chemical properties of the deposited polycrystalline films approach those of natural diamond. Free-standing diamond structures can be fabricated by etch-removal of the substrate after deposition. Using a microwave technique, researchers have produced diamond films having a thermal conductivity of 8 watts/cm deposited at rates of 10 micron/hour for a cost of about $50/carat (200 mg).

DLC films are made primarily using PECVD and single or dual ion beam techniques at low substrate temperatures. DLC films are smooth with most properties approaching those of natural diamond, with the exception of thermal conductivity which is much lower for DLC films than for natural diamond. The dual beam technique, which uses separate hydrogen-derived and methane-derived ion beams of about 125 eV ion energies, produces films that have the highest index of refraction and the lowest optical absorptance of all the low-temperature DLC deposition techniques. Thin (1500 Angstroms) DLC films are being used as abrasion-resistant coatings on infrared optics and optical products such as eyeglasses, sunglasses, and scanner windows. NASA researchers report that 1000 A dual beam-deposited DLC films transmit 85% of light at 0.5 microns wavelength.

When techniques for producing smooth, adherant diamond films are developed, it is expected that they will have extensive application in the semiconductor packaging industry because of diamond's high thermal conductivity (about 5 times that of copper) and high electrical resistivity. Diamond can also be used as a cold cathode electron emitter and as such is of interest in the flat-panel display industry. Diamond films may also provide protection to surfaces in low-earth orbit where oxygen erosion is a problem.

9.7.9 Hard Coatings

Hard coatings, formed by reactive Physical Vapor Deposition (PVD) processes, are becoming widely used in the decorative coating and tool industries.[346] Hard decorative PVD coatings are more resistant to wear and corrosion than are electroplated decorative coatings, such as gold and brass, which must use a polymer topcoat for protection. Such decorative hard coatings are being used on plumbing fixtures, sporting goods, metal dinnerware, eyeglass frames, door hardware, and other such applications where the coating is subjected to wear, abrasion, and corrosion during use and cleaning. Titanium nitride (TiN) is used for a gold-colored coating and zirconium nitride (ZrN) looks like brass. Titanium carbonitride (TiC_xN_y) can have a color which varies from bronze to rose to violet to black depending on the composition. The titanium carbonitride coatings are generally harder than the nitride coatings. Aluminum can be added to the nitrides to impart some high temperature oxidation-resistance. Chromium carbide (CrC) coatings have a silver color and are hard and oxidation resistant.

In order to get the most hard, dense, wear and corrosion resistant coating, the substrate temperature should be as high as possible and concurrent bombardment by energetic atomic-sized particles during the reactive deposition should be used (Fig. 6-11). When coating temperature-sensitive substrates such as plastics, the temperature must be kept low and concurrent bombardment can be used to densify the film. One technique for coating temperature-sensitive materials, uses the deposition of many thin layers separated by a cooling period. This is done by mounting the parts on a rotating fixture that is passed in front of the deposition source, multiple times. In one decorative application, multiple, alternating gold and TiN layers are deposited, using the same type of fixture. In this application, as the gold wears off at high points it exposes the underlying gold-colored TiN and the coating still looks gold and the article can be advertised as being gold plated.

Hard PVD coatings are also used for coating machine tools such as drills, lathe tool inserts, stamps and punches, and expensive forming tools such as injection molds for plastics. The PVD hard coating is advantageous for coating forming tools, in that the process does not change the physical dimensions of the part significantly. In many cases, the TiN coatings can be stripped from the tool surface, for repair and rework, without attacking the substrate material. This involves using a hydrogen peroxide:ammonium hydroxide:water wet etch or a CF_4:O_2 plasma etch. Generally the machine tools can be heated to rather high temperatures during deposition. For example, in coating hardened steel drills, the substrate is heated to 450°C or so before deposition is started. This preheating can be done by ion bombardment, which also sputter cleans the surface, or by using other heating sources in the deposition chamber.

Industrial tool coatings are typically 1 micron to 15 microns in thickness. In addition to being hard and dense, tool coatings should also have a high fracture toughness to inhibit fracture initiation and propagation, and possibly have some compressive stress to inhibit fracture propagation. The most common tool coatings are TiN, TiCN and $TiAlN_2$ while other coatings such as zirconium nitride, hafnium nitride, titanium carbide, and chromium nitride are less commonly used. The TiCN coatings are often multilayer structures with alternating layers having differing carbon to nitrogen ratios which increase the fracture toughness of the coating. In forming the coating, sometimes an initial "adhesion layer" of the metallic constituent of the hard coating is deposited to alloy or react with the tool surface before the hard coat material is deposited. In other cases, the tool surface is hardened by plasma nitriding before the hard coating is deposited.

The $TiAlN_2$ coating forms a continuously renewable aluminum oxide layer on the coating surface at high temperatures. This oxide helps to prevent the high-temperature degradation of the nitride and acts as a diffusion barrier that reduces adhesion between the "hot chip" and the coating in high-speed machining applications. Often carbon-containing coatings, which are dark-colored, are topcoated with the gold-colored TiN for marketing purposes. Titanium carbide (TiC) coatings are applied to aluminum surfaces to provide a hard surface for vacuum sealing applications.

The plasma gas used for reactive deposition, is a mixture of argon, nitrogen and a hydrocarbon gas such as methane. The composition of the coatings is varied by varying the gas mixture. The most common vaporization sources for the ion plating of hard coatings are unbalanced magnetron sputtering, and cathodic or anodic arc vaporization. Bombardment during

deposition is commonly achieved by applying a negative bias (-200 to -300 volts) to the substrate and accelerating positive ions to the surface from a plasma. A high ratio of bombarding ions to depositing atoms is important to densifying the depositing material. In the unbalanced magnetron sputtering source, few of the sputtered atoms are ionized but in the cathodic arc sources, a high percentage of the vaporized atoms are ionized. Since these "film ions" have a higher mass than do the gas ions, they are better able to sputter surfaces and densify films by "atomic peening." The cathodic arc source seems to produce the best coating adhesion, but a disadvantage is that the liquid globules that are formed during vaporization, generate nodules in the coating that can be dislodged during use, producing pinholes. One equipment manufacturer uses a process where an "adhesion layer" is formed by arc vaporization and the coating thickness is built-up by unbalanced magnetron sputter deposition.

Another technique for depositing TiN and TiCN uses an anodic arc source which vaporizes material from a molten evaporant using a low-voltage high-current electron beam either from a hot filament or from a hot hollow cathode. This type of source cannot be used to deposit $TIAlN_2$ films due to fractionation of the titanium and aluminum during the thermal evaporation of the Ti-Al material. Another technique uses the deposition of thin layers (few Ångstroms thickness) of the metallic constituent (e.g. titanium) and then forming the compound (TiN) by bombardment with reactive gas (nitrogen) ions from an ion source. By using multiple depositions, the coating thickness can be built up to the desired thickness.

Very thin hard coatings (< 0.1 microns) are of interest for low contact force applications such as the "flying head" on hard disc drives. Transparent hard coatings, such as diamond-like carbon and SiO_2, are also being developed to increase the abrasion resistance of transparent plastic surfaces such as those used for aircraft canopies and sunglasses.

9.7.10 PVD Films as Basecoats

The deposited films can be used as the substrate for other deposition techniques. For example, electroplating copper directly on titanium is difficult, but PVD deposited copper on titanium allows subsequent electroplating of copper to the desired thickness.[359][360] When used in this manner, the film must be stable to the chemical bath used for electroplating.[141]

9.8 SUMMARY

There are no "Handbook Values" for the properties of film material formed by PVD processing. The properties vary with a number of factors including substrate surface chemistry, mechanical properties, and physical properties; deposition process and parameters; source, system and fixture geometry; nucleation, interface formation and film growth as well as post-deposition changes in properties. In order to obtain a film with the desired properties these variables must be investigated and to have a reproducible product all of these variables must be controlled.

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10

Film Characterization and Some Basic Film Properties

10.1 INTRODUCTION

There are no "handbook values" for the properties of deposited thin films. Some authors attempt to tabulate property values but they are really what has been obtained by some investigator under conditions which are often unspecified or poorly specified with no indication of reproducibility. The properties of film are dependent on the following factors (Sec. 1.2.2):

- Substrate surface chemistry and morphology (Chs. 2 and 10)
- Deposition environment (Chs. 3 and 4)
- Deposition technique and deposition parameters (Chs. 5, 6, 7, and 8)
- Nucleation and growth of the film (Ch. 9)
- Postdeposition processing and changes (Sec. 9.6)

Characterization can be defined as determining some characteristic or property of a material in a defined and reproducible way. Some characterization techniques for substrate surfaces were discussed in

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Sec. 2.4. Characterization can be at all levels of sophistication and expense. Before spending a lot of money characterizing a film (or substrate) you should ask yourself several questions, namely:

- **No. 1—Is the processing and product reproducible?** If not then time and money are probably being wasted.
- Who will do the characterization? If someone else is doing the characterization are the right questions being asked and is the necessary background information being given?
- Who is going to determine what the results mean?
- How is the information going to be used?
- Has product variability within a lot (position-to-position in the fixture, etc.) and from lot-to-lot been considered?
- In development work, have the experiments been designed properly to provide the information needed to establish limits on the processing variables and the product properties? These limits are necessary to write the specifications for transferring the technology (App. 2).
- Who determines what is important and the acceptable limits?
- How quickly is the information (feedback) needed?
- Does the testing program consider subsequent processing, operational and environmental considerations?
- Is needless characterization being done or could simpler characterization methods be used?
- Is everything being specified in order to get the product/function desired?
- Are things being over-specifying?—i.e., specifying things that are unimportant or to unnecessary limits.
- Are the functional/reliability requirements and limits on precision and accuracy of measurements reasonable?
- Is the correct statistical analysis for your application being used? Is the sampling method statistically correct?
- Are absolute or relative (comparative) measurements needed? Precision or accuracy or both.

10.2 OBJECTIVES OF CHARACTERIZATION

The objectives of characterization of a film/coating (also processing equipment and processing procedures) during development and production can be to:

- Determine the effect of processing variables on properties of the material
- Establish satisfactory performance criteria and the limits for obtaining satisfactory performance (function, processing, service lifetime)
- Establish a baseline for satisfactory performance—i.e., when things go bad, you will have something to compare
- Monitor process and material reproducibility
- Assist in failure analysis
- Determine the stability of the functionality of the film

10.3 TYPES OF CHARACTERIZATION

Film (and substrate) characterization can consist of determining one or more properties such as:

- Elemental composition—surface, bulk, trace, distribution, variation with position
- Chemical state—chemical bonding: distribution and degree
- Stoichiometry of compounds
- Structure and microstructure—crystallography (phase), orientation, grain size, lattice defects
- Morphology—surface, bulk, local, microporosity
- Physical properties—density, surface area, thickness
- Mechanical properties—elastic (Young's) modulus, yield stress, fracture toughness, hardness, wear resistance
- Electrical properties—resistivity, dielectric constant, carrier mobility & lifetime

- Optical properties—optical adsorption, index of refraction, reflection, color
- Chemical properties—corrosion, etch rate, catalytic properties
- Barrier properties—permeation, diffusion
- Behavorial properties—response to subsequent processing and operation
- Stability properties and failure modes
- Local properties—pinholes, morphology
- Other functional properties—bondability, electrical contact resistance
- Other—adhesion to surfaces, recontamination rate and contaminant retention, residual film stress, etc.

Properties may be general, such as thickness, or may vary locally such as the presence of pinholes in the film or small areas of high film stress. The general properties of the film may not be uniform over a large surface area or may not be constant from one area to another on the holding fixtures (i.e., there may not be position equivalency). Often variations may be due to substrate conditions, deposition parameters, etc. This means that some care must be taken in selecting the material to be characterized and the sampling statistics must take into consideration the possibility of such variations with position.

10.3.1 Precision and Accuracy

Measurements can be precise or accurate or both. Precision is the ability to reproduce a value. This means that there will be little scatter among a number of readings. Accuracy is how close the values are to some absolute (correct as referenced to a standard) value. How the measurements are to be used determines the type of measurement to be made and whether it needs to be accurate or not. For example, when the measurement is used in production to determine if the product being produced today is like that yesterday, a relative value is often used and precision is the desirable attribute. If the measurement is to be incorporated into specifications and to be use for the transferring technology between machines or facilities then an accurate value should be determined.

Accuracy usually means instruments that are calibrated by using a primary or secondary standard and/or comparative samples that are carefully calibrated. A measured value can be precise but not accurate. In many cases, the reported value should be determined by collecting a number of measured values and determining the mean value. This gets into the area of statistical measurements and their meaning.

10.3.2 Absolute Characterization

Absolute characterization means an accurate value such as: specific elemental composition (weight percent), the resistivity (ohm-cm), the thickness (microns, angstroms, nanometers) etc. In order to get absolute values it is often necessary to compare to standards for the measurement of interest. This may increase the cost of the measurement significantly and can require appreciable time and the feedback may be slow.

10.3.3 Relative Characterization

Relative (comparative) characterization means a comparison of some property such as color, reflectivity electrical resistance, or composition, to a known sample or value such as one that has been characterized in an accurate manner or one that has been shown to provide satisfactory performance. Often precision is the most desirable attribute of a measurement for comparative purposes. Relative evaluations are generally more easily obtained and are less costly than are absolute values and are often used for process monitoring and control, and to control process/product reproducibility.

10.3.4 Functional Characterization

Functional characterization is related to the final use of the material and are such properties as: adhesion, electrical resistivity, hardness, optical adsorptance, color etc. Subsequent processing, storage and service may alter the functional properties and these possibilities must be evaluated.

10.3.5 Behavorial Characterization

Behavorial characterization refers to non-functional properties which may be important in use or to indicate possible changes in film properties. Examples are: wetting angle, optical reflectance as a function of viewing angle, chemical etch rate, etc. Stability properties refer to those concerned with the response of the material to subsequent use, storage, or use. For example, do the properties change under an elevated temperature or is the material corroded by a subsequent processing or service environment?

10.3.6 Sampling

Property measurements may be made with all levels of sophistication, at various stages in the processing and with various objectives. Properties may be measured on 100% of the product, which is unusual, or may be done on a portion of the samples coated, or may be done on special samples ("witness samples"). For example, thin substrates that can be deformed by film stress are used to measure residual film stress, and smooth surfaces are masked to provide "steps" for stylus-type thickness measurements. In some measurements, such as those used for adhesion tests or stress measurements, it is very important that the witness samples be of the same material as the substrates and processed in the same manner as the substrates. In cases where different materials, surface conditions (smooth vs rough for instance) or processing is used for the witness plates, the effects of the differences should be determined. When depositing on a large area or on a number of samples, position equivalency needs to be established as part of the sampling program. Position equivalency may mean determining which fixture positions represent the extremes and making sure that these extremes lie within the acceptable limits.

In many cases, testing will destroy the sample as far as subsequent processing is concerned. If the film is to be used, testing, or the handling associated with testing, will contaminate the film and the film may have to be cleaned before subsequent processing. Testing can also leave undesirable residual on the surface that can affect film stability. For example, the tape test can leave residual chlorides on the surface of aluminum films that can lead to long-term corrosion of the film.

10.4 STAGES AND DEGREE OF CHARACTERIZATION

Characterization of film properties can be done at various points in the processing. Early characterization can give an early indication of problems or variations in the processing. Many characterization techniques require destruction or signification modification of the sample. In some cases, evaluations can be made by non-destructive evaluation (NDE) and then used. Examples include: 4-point probe resistivity measurements, adhesion—tensile pull to value, thermal transmission, and Rutherford backscatter (RBS) analysis.

10.4.1 *In Situ* Characterization

Some film properties can be measured during the deposition process or before the sample is exposed to the ambient environment and these are called *in-situ* measurements. These properties are often used for real-time process monitoring and control. Such measurements include:

- Optical thickness—measured by the amount of transmitted or reflected light and is used to control the deposition of optical coatings[1]–[3]
- Mass—measured by the frequency change of a quartz crystal oscillator;[4]–[6] used to control the deposition rate and the "thickness" of vacuum deposited films by assuming a film density.
- Electrical resistivity—by monitoring the electrical resistance of a deposited conductor stripe. The stripe is usually generated using a deposition mask.[7]
- Residual film stress of a thin wafer during deposition by deflection of a thin beam.[3][8]

The result of *in situ* characterization should be noted on the Traveler.

10.4.2 First Check

When the deposition system is first opened to the ambient environment much can be learned about the properties of the deposited film by carefully looking at the surfaces while the substrate(s) is still in the fixture This characterization is called the "first check." Things to look for include:

- *Do all the samples or all areas on a large sample look the same* (i.e., is there position equivalency?).
- *Color*—is it like it should be? Color is often a sensitive indicator of composition and surface morphology.
- *Is the color uniform*? The eye is a very sensitive color-comparison instrument.
- *Angle-dependent optical effects*—optical effects which vary with angle-of-view are often due to surface morphological effects.

The results of the first check should be noted on the Traveler.

Note: In production, this is often an overlooked opportunity. The production operators should be trained to look for variations from run-to-run and the travelers should reflect this observation to remind the operators. After the samples have been removed from the fixture it is often difficult to find where they came from. See footnote in Sec. 9.4.1.

10.4.3 Rapid Check

Some simple, rapid, and cheap property measurements can provide a measure of the process and sample reproducibility immediately. Some properties which sometimes can be easily qualitatively or quantitatively determined include:

- *Electrical resistivity*—by 4-point probe measurements
- *Thickness*—by stylus or optical interferometry
- *Adhesion*—by pull test, bad breath test (Sec. 11.4.7), tape tests
- *Film stress*—bending of thin beam or disk that has accompanied the substrates
- *Optical properties*—color, reflectance, extinction coefficient
- *Chemical etch rate*—time for film removal/weight loss
- *Composition by x-ray fluorescence*
- *Light transmission* (backlighting of the film on transparent/translucent substrates to show pinholes, film thickness uniformity

- *Porosity test*
- *Oblique lighting*—shows bumps and particulates

Often one characterization technique will yield results that depend on several properties of the material. For example: a chemical etch rate test will give an indication of density, surface area, porosity, and composition and is an excellent relative (comparative) test to determine if the product today was the same as it was yesterday.

Often these simple observations provide the first clue to a problem or change in the processing and often to the origin of the problem. Remember, properties should have been previously determined for a "good" product so that there is a baseline value with which to compare. Property and compositional measurements often provide an average value and local property variations such as pinholes, stress, thickness may be missed—are they important?

10.4.4 Postdeposition Behavior

After the samples have been removed from the fixture some properties may be monitored as a function of time such as:

- *Color change with time*—may be due to oxidation, absorption of contaminates
- *Weight change with time*—absorption of contaminates, corrosion
- *Changes of electrical resistivity* (sheet resistivity) or *temperature coefficient of resistivity* with time—may be due to oxidation of columnar surfaces

Some postdeposition treatments or subsequent processing can lead to property changes which will be indicative of the properties of the as-deposited material. Such treatments include:

- *Heating* which can cause oxidation, diffusion, void formation
- *Chemical treatments* which can cause oxidation or etching.

10.4.5 Extensive Check

Extensive characterization is generally time-consuming and expensive with a slow feedback time. Examples are the use of surface analytical spectroscopies (Sec. 2.4.1) and when samples are sent elsewhere for analysis. Care must be taken that the storage and transport do not introduce artifacts into the analysis. For example, adsorption of hydrocarbons on the surface during storage and transport can appear as a carbonaceous contamination in Auger Electron Spectroscopy (AES) analysis and you would not know where it came from. In some cases, elaborate analytical instrumentation can be used in the deposition system or on the production line. For example, in epitaxial growth, RHEED (Reflection High Energy Electron Diffraction) is used in the deposition chamber to monitor crystal growth during deposition and SEM (Scanning Electron Microscopy) is used on semiconductor device production lines to look at conductor stripes after etching.

10.4.6 Functional Characterization

Functionality is the property of the film that is to be used, such as electrical conductivity, corrosion resistance, color etc. In many cases, the functionality of the system must be determined in the context in which the film is to be used. For example, the perception of color depends on the illuminating source—what looks one color under fluorescent lighting will look different in the sunlight. Some properties may change with subsequent processing, time or service and this should be considered.

10.4.7 Stability Characterization

The best test of stability is the "operational life-test" where the film is used as it would be in service and samples are tested periodically to determine any degradation.[9] Since this means a long test period, it is often desirable to used "accelerated life tests" where the degradation mechanism is accelerated by increasing the temperature (e.g. diffusion processes), chemical concentration (e.g. corrosion), mechanical movement (e.g. fatigue failures), etc. Determining what should be accelerated and by how much without changing the response mechanism is a chancy business. For example, see footnote in Sec. 9.6.6, where the difference in

coefficients of thermal expansion between an encapsulated film and the substrate caused tensile stresses which caused voids to form in the film on storage at room temperature. Trying to accelerate this effect by raising the temperature would relieve the stress. A better acceleration condition in this case, might be to add mechanical stress (by flexing the substrate) to the existing residual film stress.

A comparison between the accelerated tests and the operational life tests provides an "acceleration factor." A major concern in accelerated life tests is to be sure that you are accelerating the right degradation mechanism. Most often both life tests and accelerated tests are run. In addition, "control samples" (shelf samples or archival samples) are kept in pristine condition so that aged samples can be compared to the original materials. This type of test has the added advantage that there is an archival sample to compare to if failure analysis must be performed in the future.

10.4.8 Failure Analysis

Characterization techniques are often used in failure analysis. There are many ways to approach failure analysis. Generally there is a great deal of detective work involved. This means determining the failure mode(s), deciding what might cause the failure, whether this failure is symptomatic of all the material produced or whether it is a "sport" that is an anomaly, etc. Often it means going back to the specification, MPIs and travelers to determine if there was a change in processing.

In failure analysis, comparisons to other samples is often invaluable. It is therefore highly desirable to have archival samples that have not seen service conditions. It is quite common to find that archival samples have been disposed of during "clean-outs" and this adds problems to the failure analysis.

10.4.9 Specification of Characterization Techniques

Methods of characterizing the sample should be carefully specified. If suitable standards for the characterization techniques can not be found, then reproducible characterizing procedures will have to be developed and carefully specified.

10.5 SOME FILM PROPERTIES

10.5.1 Residual Film Stress

Invariably atomistically deposited films have a residual film stress which may be tensile or compressive and can approach the yield or fracture strength of the materials involved (Sec. 9.4.6).[10][11] These stresses can be composed of stresses that arise from the differing coefficients of thermal expansion of the film and substrate when the deposition is performed at elevated temperatures, growth stresses due to the atoms not being in their most energetically favorable position (quenched-in), and stresses due to phase changes in the film material after deposition. These residual stresses are very sensitive to substrate configuration and fixture configurations and motion as well as the deposition parameters.[12][13] The total stress in the film is determined by summing the stress level, which can vary through the film thickness, through the film thickness.

Lattice strain is caused by the residual film stress and represents stored energy. The lattice strain of the film material can be measured by X-ray diffraction lattice parameter measurements.[14] This strain measurement can then be translated into a stress by assuming the mechanical properties of the material. This technique may not give the same value of stress as measured by deflection techniques since it does not sum over all the stresses (those associated with the grain boundaries for instance) and it sees lattice strain over small regions (such as in columns) that may not add to the cumulative stress.

The deflection of a thin narrow beam by the film stress is the most general technique for measuring film stress. The beam deflection can be measured using interferometry, an optical lever using a laser beam or by capacitance measurements. The beam can be allowed to bend during the deposition or be constrained from bending during the deposition. There are different calculations for the two cases. If the thickness of the film is small, then the modulus of the film material is immaterial, however, measurements can also be made if the mechanical properties of the substrate and/or the film are unknown, by mechanically loading the beam and making deflection measurements.[15]

The force on a substrate due to the film stress is a function of the film thickness with the force generally proportional to the thickness although there is generally a stress gradient in the film. The film morphology affects the stress buildup with a columnar film morphology

(low density) often resulting in a low total stress. Film stress is an important factor in the adhesion and stability of films. High isotropic compressive film stresses produce "blistering" of the film from the surface in "worm-track" patterns.[16][17] High isotropic tensile film stress produces microcracking of the film. The cracks tend to meet orthogonally and form polygon "islands" or "chips" such as are seen in dried "mudflats" (Fig. 11-3).[18]–[21]

If the compressive stresses are highly anisotropic, the "worm-track" pattern changes to line-shaped blisters. If the tensile stresses are highly anisotropic, the "mud-flatting" pattern changes to linear cracks. If the adhesion between the film and the substrate is high, the stress can cause fracture in the film or substrate material rather than at the interface. The film buckling or cracking may be time dependent and depend on the moisture available in the ambient environment (static fatigue). If the substrate is ductile, the fracture of the film will be different.[22]–[26] Fractures and fracture patterns in films can be detected optically, with an SEM or by the use of fluorescent dye adsorption.[27][28] Generally residual film stress should be minimized to prevent long-term failure.[29][30]

Film stress generally will change with film thickness. Stress gradients can exist in the deposited film due to the growth mode and differing thermal histories of the various layers of the film. The film stress gradients leads to "curling" of a film when it is detached from the substrate.[31] If the adhesion failure is such that some of the substrate material remains attached to the film, the film will curl because of the constrained surface. For example, a chromium film on glass can have a high anisotropic tensile stress. When there is adhesion failure, the fracture can propagate in the near-surface region of the glass leaving a thin layer of glass on one side of the film. This will cause a stress gradient and the film will curl-up with the glass layer on the convex side.

Localized regions of high intrinsic stress can be found in films due to growth discontinuities or defects such as nodules or surface features such as hillocks. These stressed areas can lead to localized adhesion failure under applied stress giving pinholes in the film and flakes that can become particulate contamination in the deposition chamber (pinhole flaking).

When the angle-of-incidence of the depositing atom flux is not isotropic, the energetic bombardment flux is not isotropic, or there is a texture to the surface features, an anisotropic film stress may be produced.[13] Figure 10-1 shows the interferometric patterns produced by isotropic stress, non-isotropic stress and stress which is compressive in one direction and tensile in the other.[15]

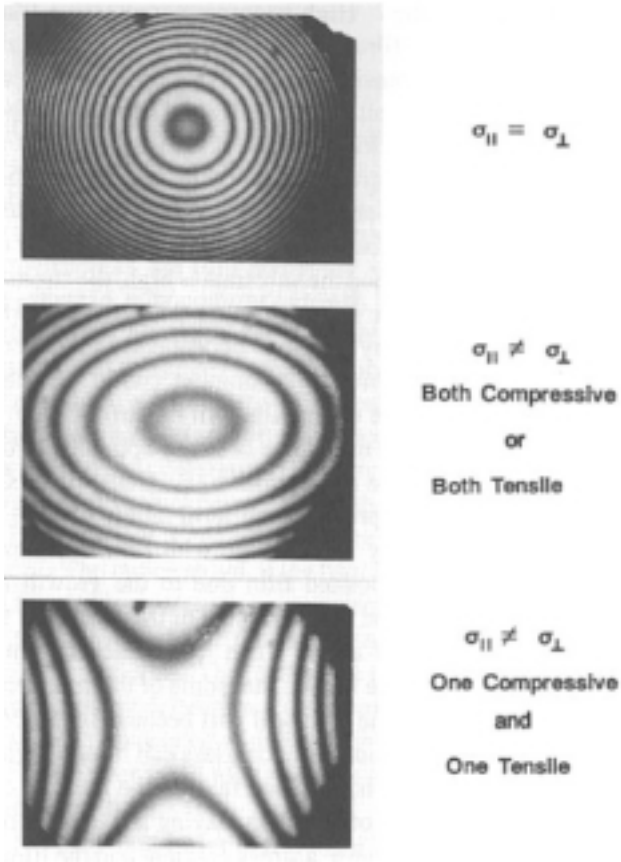


Figure 10-1. Interferograms of stressed and bowed films.

On a long, narrow and thin substrate (beam) the sum of all the stresses in the film causes the "beam" to bend. From the degree of bending and the mechanical properties of the substrate (and of the film if it is thick), the film stress (σ) can be calculated. Figure 10-2 shows a sample calculation.

If the beam is not sufficiently narrow then there will be an "angle-iron" effect where bending in the narrow direction will cause stiffening of the beam. Typically a width to length ratio of 1 to 10 is sufficient to minimize this problem unless the stress level is very high. The bowing of a disk is a special case for the semiconductor industry where the film is deposited on a circular wafer.

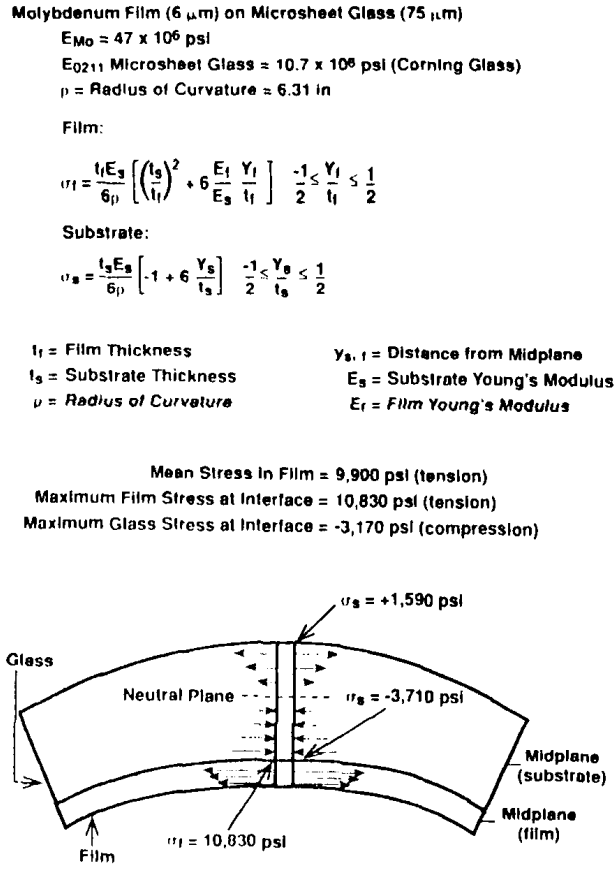


Figure 10-2. Sample stress calculation for the film stress (σ_f) and the substrate stress (σ_s).

10.5.2 Thickness

There are many direct and indirect techniques for measuring the thickness of a deposited thin film.[32][33] A general problem in measuring film thickness is the definition of the "surface." Since films have a low thickness, substrate surface roughness can play a major role in the thickness measurement. Film and coating thickness may be defined in three ways:

- *Geometrical thickness*—measured in mils, microinches, nanometers, angstroms, or microns and does not take into account the composition, density, morphology, microstructure, etc. Location of the surface and interface must be determined and surface morphology of the substrate is a factor.

- *Mass thickness*—measured in micrograms/cm^2 and can become a geometrical thickness when the film density is known or assumed. Does not take into account the composition, density, microstructure, etc. Surface morphology is not a factor.
- *Property thickness*—measures some property such as X-ray absorption, X-ray fluorescence, beta (electron) backscatter, or ion backscattering and can become a geometrical thickness by knowing property-thickness relationships which are usually determined by calibration. Thickness measurement may be sensitive to density, composition, crystallographic orientation, porosity, etc.

Different thickness measuring techniques may give differing values for the thickness. Many of the indirect thickness measuring techniques require careful calibration. Often thickness is determined by depositing the film on a smooth substrate (witness plate) in an equivalent position and determining the geometrical thickness. Since the growth and geometric area on the witness plate is different from that of the real substrate, the thicknesses may differ but the measurement is good for relative values from run-to-run.

Thickness measuring techniques can be categorized as contact and non-contact techniques. Contact thickness measuring techniques measure a defined step height. The step from substrate to film surface can be generated by masking during deposition or by postdeposition etching. The most generally used technique is the surface profilometer (stylus technique) which can scan a length of several centimeters with a horizontal position resolution of <0.2 microns and give height measurements of <20Å and up. In order to get high accuracy and precision with thickness measurements utilizing step heights, it is necessary to control the temperature of the substrate/film during the measurement.

Non-contact thickness measuring techniques do not touch the film surface. Optical techniques using interferometry across a step from the substrate to the film surface, are the most common non-contacting techniques. The interferometry techniques can measure step heights down to 10Å and up to several microns. Color comparison is another type of interferometric measurement which uses constructive and destructive interference through a transparent film to determine film thickness from a few hundred Angstroms. Ellipsometric film thickness measurements use

rotation of polarization axis through a transparent film (oxide films) and can measure film thickness from a few Angstroms to few microns.[34][35] Ellipsometry can be used as an *in situ* measurement technique for some applications.

Non-contacting techniques can use stylus movement to determine the height of a feature such as a step. Atomic Force Microscopy (AFM) uses deflection of a beam under attractive forces to measure the height.[36] Scanning Tunneling Microscopy (STM) uses electron tunneling to determine the step height.

By knowing the property-thickness relationship, X-ray (*ASTM B 568-79*) and optical adsorption can be used to measure thickness. This is most often used as a comparative technique. The thickness property relationships also allows emission and backscatter techniques to be used for thickness measurement. These techniques include x-ray fluorescence (XRF) (Sec. 10.5.10a),[37][38] backscatter of low energy (10 keV) electrons, and backscatter of high energy ions such as used in Rutherford Backscattering Spectrometry (RBS) (Sec. 10.5.10b).

In beta (electron) backscatter thickness measuring techniques, electrons from a radioactive source directed on to a surface and the backscattered electrons over a given period of time are measured by a geiger counter. This technique requires calibration. The thickness range measured depends on the source and scattering material. This measuring technique is generally used for thick deposits. In magnetic eddy current techniques, oscillator coils above and below the film on an insulating substrate induce magnetic fields in the film, energy is dissipated, and the oscillator is loaded. The amount of loading depends on the electrical conductivity of the film. This technique is primarily used on thick deposits.

10.5.3 Density

The mass density of a thin film is measured in grams per cubic centimeter or the aerial density can be given in micrograms per square centimeter. The density depends on:

- Composition
- Arrangement of the atoms
- Closed porosity (void) volume
- Definition of the surfaces

A less than fully-dense material may mean: that there are voids in the material, there is foreign material in the film, or the material is not stoichiometric. A deposited material may easily have several atomic percent of foreign material incorporated into the lattice or may easily be off-stoichiometry by an appreciable amount .

Film density can be measured using geometry-property relationships or by displacement-floatation techniques. In the geometry-property techniques, the volume or area of the sample is determined as well as the mass of a specific volume or area. From this, the density can be calculated directly. For example, aluminum, which has a bulk density of 2.7 g/cm^3, will form a film with an aerial density of 27.0 micrograms/cm^2 for a 1000Å film. Some bulk densities (g/cm^3) of common inorganic compound film materials are: SiO_2 = 2.20 and TiN = 5.29. Problems arise over determining the thickness of a thin film.

The film may be removed from the substrate and the density determined by displacement techniques.[39] Pycnometry involves the displacement of a liquid or gas from a container of accurately known volume and the weight of the sample. Density gradient columns utilize a thermal gradient to produce a density gradient in a liquid. The sample will float at a level of the same density fluid . Calibration floats are used to determine the density. Fluids having densities up to 3.3254 g/cm^3 (methylene iodine solution) are available. The most accurate techniques have been developed to study radiation induced void formation in metals and utilizes hydrostatic weighing (in and out of a fluid) of small samples (30 mg) with a microbalance to a precision of 0.04%.[40]

10.5.4 Porosity, Microporosity, and Voids

Generally porosity is not desirable in a film. The porosity in a deposit can consist of open porosity where the pores are interconnected, closed porosity where the pores are isolated and not interconnected and through-porosity (pinholes) where the pore extends through the deposit from the surface to the interface. Typically a deposit will contain both open and closed porosity to some extent. A material with closed porosity will show a decrease in density while a material with open porosity may or may not, depending on the measurement technique. Voids is another term used for isolated pores while microvoids is the term used for very small voids down to clusters of lattice vacancies (a few angstroms in diameter) (Sec. 9.4.4). Microvoids may be aligned to give microporosity through the

film. This microporosity is generally along grain boundaries and column boundaries in the film.

Voids in the bulk of the material form by the growth processes or by agglomeration of defects during or after deposition. Porosity may affect film properties in a number of ways. The high surface area in a porous material results in a high chemical etch rate, a high corrosion rate, easy contamination with difficult cleaning, dependence of some film properties on surface effects such as oxidation, and excessive deformation under load. In dielectric materials, voids decrease the index of refraction. Voids in materials are typically measured and studied by density measurements, Transmission Electron Microscopy (TEM), and etch rate (comparative) analysis. In TEM the sample is thinned and the voids are observed directly by using the "underfocus"-"overfocus" technique.[41] Voids as small as 7Å in diameter can be resolved using this technique.

If voids exist at the interface between the coating and substrate they may reduce the adhesion by decreasing the effective contact area, acting as stress concentration defects and provide an easy path for fracture initiation and propagation (Ch. 11). Interfacial voids also results in increased contact resistance between film and substrate, decreased thermal conductance across the interface, and presents a discontinuity to stress wave propagation. Voids at the interface may be formed by the growth process during interface formation, by the accumulation of defects by mass transport processes or by the loss of material by diffusion. Voids at the interface are evidenced by low adhesion, high contact resistance, and possibly low thermal conductivity. Interfacial voids are studied by careful TEM sample preparation and by surface analysis of the failure surfaces after failure.

Through-porosity (pinholes) in conductive films may be measured by:[42][43] corrosion potentials (anodic polarization),[44] colorimetric imaging, electrographic printing, selective dissolution, and by corrosion products decorating the pinholes as shown in Fig. 10-3. The corrosion potential technique uses the galvanic corrosion potential formed between the exposed and non-exposed surfaces when in a corroding electrolyte. The corrosion potential depends on the area-fraction of the exposed surface and the anodic polarization on the exposed surface. For a metal surface covered by a noble-metal coating with low porosity, there is a linear relationship between the corrosion potential and the area-fraction of the pores.

Colorimetric imaging allows the pinhole density and location to be mapped over a surface. For example, in Cr-Au metallization, porosity in the gold can be colorimetrically imaged by exposing the metallization to

fuming hydrochloric acid (HCl) then covering the surface with dephenylcarbizide in gelatin-glycerine made fluid by heating. When the gel is poured over the surface, it hardens, and the dephenylcarbizide reacts with the chromium to produce a colored spot on the film. The film can then be peeled from the surface giving a picture of the porosity.

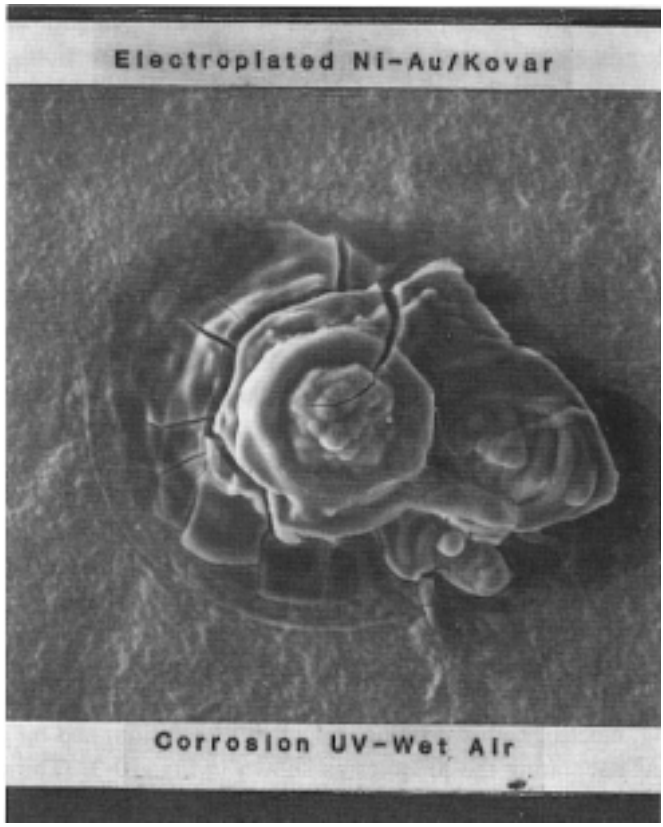


Figure 10-3. Pinhole corrosion.

Porosity or cracks through metal films on metal substrates may be measured by electrographic printing where a chemical solution in a paper or gel is placed in contact with the film, and a copper electrode is placed behind the paper. The electrode acts as the cathode and the substrate is the anode and a current is passed through the system (typically

200 mA, 30 sec). The paper is then observed for spots which indicate that some of the substrate material has reacted with the chemical solution. Table 10-1 lists some electrographic printing reactions.

Table 10-1. Electrographic Printing

Deposit	Reagent solution	Indication
Au on Cu	Potassium ferricyanide	Brown spots
Ag on Cu	Potassium ferricyanide	Brown spots
Sn on Fe	Potassium ferricyanide	Blue spots
Au on Ni	Ammoniacal dimethyiglyoxime and sodium chloride	Red spots
Cr on Ni	Dimethylglyoxime	Pink spots
Cu on Fe	Dimethylglyoxime	Deep cherry red spots
Ni on steel	Sodium chloride + hydrogen peroxide	Rust spots
Zn or Cd on Steel	Sodium hydrosulfide	Black spots

Porosity through thin dielectric films on metallic substrates may be measured by corrosion (liquid gas), selective chemical dissolution (electrographic printing—solution analysis), electrochemical decoration, anodic current measurement, gas bubble generation (electrolytic), liquid crystal (electric field) effects, and absorption (dyes—liquid or gaseous radioactive material).

10.5.5 Optical Properties

Optical properties of films include:[45] index of refraction, reflectance, and absorptance which are a function of the wavelength, extinction (absorption) coefficient, optical scattering, index of refraction, and

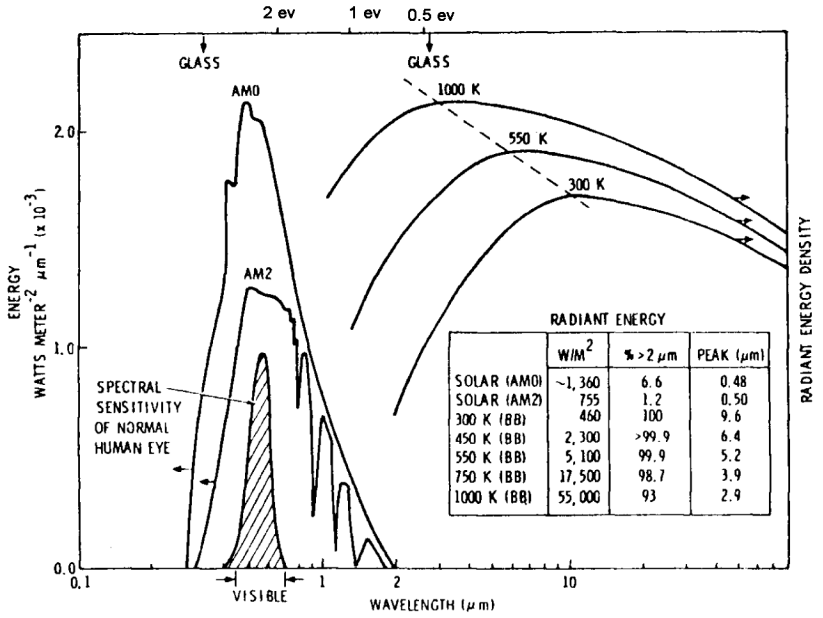
color. Optical absorption is an important effect for films used in high power laser technology where high or non-uniform absorption can give local failure of the coating.

Optical Reflectance and Emittance

Reflecting coatings reflect the incident radiation and what is not reflected is absorbed or transmitted. If there is spectral reflectance the surface is a mirror. If there is scattering, the surface is a diffuse reflector like a white paint. For deposited metal films, the difference is generally the surface finish—a smooth surface is necessary to make a good mirror.

Figure 10-4 shows the optical spectrum of solar radiation (AM0), the solar spectrum after it has passed through two standard air masses (AM2) and the optical sensitivity of the human eye which ranges from 4500 Å to 7000 Å.[46] The diagram also shows the radiant energy from black-body surfaces at various temperatures. Most of the incident solar radiation is out of the range of human vision (61% AM2) either in the long wavelength (>7000 Å) infrared region (53% AM2) or the short wavelength (<4500 Å) ultraviolet region (8% AM2). Artificial lights such as tungsten filament lamps emit a higher percentage of their radiation in the infrared than in the solar spectrum. The emission from halogen lamps and the new sulfur lamps, more nearly approach the solar spectrum.

Figure 10-5 shows the reflectivity of metal surfaces. Aluminum (Al) and silver (Ag) are the most common reflector materials and gold (Au) is a good reflector in the infrared. A highly-reflective white paint is shown for comparison. A good metallic electrical conductor will completely reflect all of the incident radiation if it is about 1000 Å thick. A thinner film will let some of the radiation pass through to the underlying material. Metallization of a glass mirror can be done on the "back surface" or the "front surface". If the metallization is on the back surface, there is some distortion and some radiation is lost in passing through the glass to and from the metallization, therefore a front surface mirror is a more efficient reflector. If the metallization is on the back surface it can be protected by a protective coating and silver is often used. However if the metallization is on the front surface, without a topcoat, it is exposed to corrosion and aluminum is the preferred material. Aluminum reflecting surfaces are often given a topcoat to provide abrasion resistance as well as enhance corrosion protection.



	W/M^2	% > 2 μm	PEAK (μm)
SOLAR (AM0)	~1,360	6.6	0.48
SOLAR (AM2)	755	1.2	0.50
300 K (BB)	460	100	9.6
450 K (BB)	2,300	>99.9	6.4
550 K (BB)	5,100	99.9	5.2
750 K (BB)	17,500	98.7	3.9
1000 K (BB)	55,000	93	2.9

Figure 10-4. Optical spectrum of solar radiation, the radiation from a hot surface (black body), and the sensitivity of the human eye.

Mirror surfaces can be overcoated with a few or many transparent coatings ("optical stacks") to further define the flux of radiation that is reflected, and the radiation that is adsorbed by using optical interference effects. An optical stack of films consists of alternate layers of film material of specific thicknesses having high and low indices of refraction.[47][48] For example, by designing the optical stack so that the infrared is not reflected (i.e. adsorbed) a "cold mirror" can be produced that minimizes the reflected heat from the light source. Such reflectors are used in light sources for hospital operating rooms and movie studios.

A reflective surface can be overcoated with transparent or semi-transparent polymer coatings that have color and/or texture, and these are often used for decorative coatings. For example, a zinc die-cast lamp base, which has a rough surface, is flow-coated with a polymer basecoat to give a smooth surface, metallized with aluminum to give a reflective surface and then topcoated with a colored lacquer to give a reflective, colored

decorative finish to the lamp base. A molded polymer bottle cap can be coated with aluminum and a lacquer topcoat to give a decorative coating. Metallized molded polymers are used as reflectors such as the auto headlight reflectors used with halogen light sources.

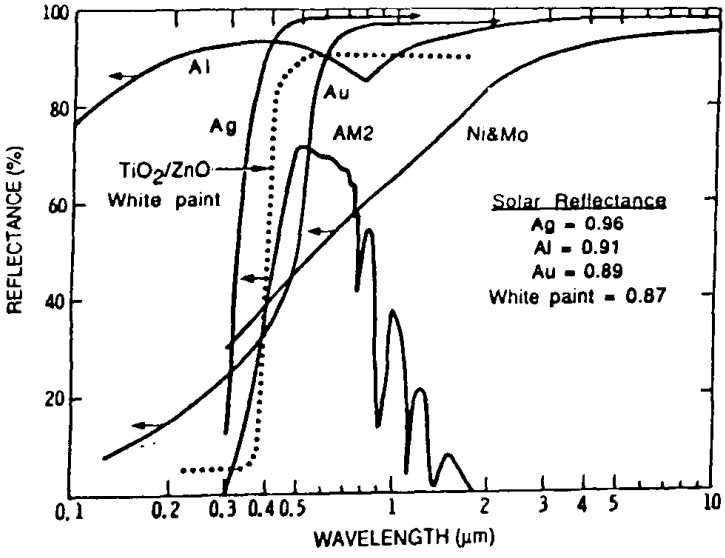


Figure 10-5. Reflectivity of metal surfaces.

Mirrors can also be overcoated with an electrically-active optical stack which can be made to be transparent or absorbing to varying degrees, by the application of an electric field. These types of optical stacks are call "electrochromic" coatings. Electrochromic coatings are composed of an ionic conductor (solid electrolyte) layer such as hydrated SiO_2, and an electrochromic material such as tungsten oxide, sandwiched between transparent electrical conductor films such as Indium-Tin-Oxide (ITO). When a voltage is applied across the sandwich, ions from the electrolyte enter the electrochromic material changing its transmittance. When the potential is reversed the ions leave the electrochromic material thus restoring the transmission. Such electrochromic mirrors are available as anti-dazzling rear-view mirrors for automotive use.

The amount of incident power scattered by a surface as a function of angle is measured by scatterometry[49] (Sec. 2.4.4e). This is normally done using a laser beam as the incident source and a detector that is moved in increments in a plane or sphere to determine the reflected power as a function of angle.

Color

A wide variety of colored films can be deposited by the PVD film deposition processes. Color is generally quantified using the parameters L*, a* and b* where L* is the luster or brightness of the coating, a* is the color content from green to red and b* is the color content from blue to yellow.[50] Typical color components for various deposition techniques are given in Table 10-2.[51]

Table 10-2. Color Coordinates for Bulk Materials and Deposited Films[49]

For some bulk materials:

Composition	Color	L*	a*	b*
TiN	golden yellow	77–80	2–5	33–37
TiC_xN_{1-x} (x<0.2)	red-gold	66–79	5.5–16	21–33
ZrN	golden green	86–89	(-3)–(-1)	23–25
ZrC_xN_{1-x} (x=0.2)	golden	79–84	(-1)–3	17–29
Au - 10K	golden	81–86	(-1.6)–1	19–30
Au - 24K	gold	88–91	(-3.7)–1	27–34

For some materials deposited by the indicated PVD deposition process

Process	Composition	L*	a*	b*
Sputter deposition	TiN	75–77	3–8	25–35
Ion plating	$TiN_{1.05}$	74–80	0.5–10	20–30
Cathodic arc Deposition	TiN	77–80	2.5	33–37
Electrodeposited	Au - 10K	81–86	(-1.6)–2.0	25–35

The color of a film can be influenced by the composition and surface morphology of the film. For example, a small amount of carbon co-deposited with ZrN makes the brightness of the color of the film more closely resemble the brightness of polished brass. A rough surface morphology decreases the apparent brightness of the surface.

10.5.6 Mechanical Properties

The mechanical properties of films are important in their response during subsequent processing and to mechanical stresses.[52][53]

Elastic Modulus

The Young's modulus (elastic modulus) of a material is the stress versus strain for the material under elastic (reversible) deformation. Often it is impossible to separate the film from the substrate without altering its properties so the measurements must be made on the substrate.[54][55] This often influences the properties being measured. Mechanical property measurements of films on substrates are made using the beam deflection techniques discussed under stress measurement except that the beam is loaded with known weights and the deflection is measured with the stress as the known.[15] Measurements can only be made as long as the film does not microcrack (tension) or blister (compression).[56] Thin films have been shown to have very high elastic modulus and strength, presumably due to surface pinning of mobile defects (dislocations). Indentation test can be used to determine the elastic properties of coatings.[57]

If the film can be separated from the substrate, the mechanical properties can be measured by microtensile techniques. By opening a hole through the substrate to the bottom of the film, a bulge technique can be used to measure the tensile properties of the film. By measuring the deformation, the mechanical properties of the film can be determined. For example, films of Al-1%Si were removed from an oxidized silicon substrate and the mechanical properties measured.[58]

The ductility of coatings can be determined using a 4-point bend test[59] as well as loading the beam and measuring creep at high temperatures.[56] This test also provides the strain-to-fracture if a method, such as acoustic emission, is used to detect crack formation and propagation in the coating.

Hardness

Hardness is not a fundamental property of a material, it depends on how it is measured (Sec. 2.4.5). The hardness of a material is usually defined as the resistance to deformation and is usually measured as the permanent deformation of a surface by a specifically shaped indenter under a given load.[60] This does not give an indication of the plastic deformation associated with loading. The hardness of a material may be influenced by the grain size, dispersed phases, defect structure, microstructure, density, temperature, deformation rate, etc. For films and coatings there may be substrate influences on the deformation which affect the measurements.[61] As a rule, the coating should be ten times the indentation depth to obtain meaningful results. Surface effects may also influence the measurements for thin films, particularly those with oxide layers.

Special techniques to measure the microhardness use microindentation techniques.[62]–[65] In addition to hardness, the elastic properties of the material can be determined from the maximum penetration depth compared to the residual depth of the indentation after the indenter has been removed.

Wear Resistance

Wear is the deformation and material loss of a material in moving contact with another material.[66] Erosion is the deformation and material loss of a material under impact. Wear and erosion of a film can be measured by: weight loss, material transfer, and wear scars. Wear is extremely sensitive to the application, temperature, materials, etc. so most wear tests are functionality-type test.[67][68] Some wear tests are:

- Pin-on-disk
- Ball-on-disk
- Ring-on-block
- Taber abrader
- Falex tester
- Tool wear
- Particulate erosion

A specific form of wear is that of tool-life, where a coated tool surface is used to machine a metal and the tool velocity, pressure, and

contact distance (revolutions) are used as variables.[69] Fretting (adhesive) wear is encountered where materials slide against one another and adhesion between the surface is important to the wear mechanism. This type of wear is encountered in electrical connectors and affects contact resistance. Fretting is of particular concern at high temperatures and when metals lose their natural oxide layers. Wear and surface composition may be studied *in situ* in the scanning electron microscope by the use of appropriate fixturing.[70] These wear studies can also contribute to contact resistance studies particularly when light contact loads are used.

Friction

Friction is not a fundamental property of a material—it depends on how it is measured.[66][71] Friction can either be static (starting) or dynamic (moving). Friction is very sensitive to the surface chemistry,[72] hardness, and morphology. Friction is measured using surfaces in contact with varying load moving over surfaces and the friction is measured using a load cell. The coefficient of friction is given by the ratio of the moving force to the applied load. The most common configuration is a pin-on-disk.

10.5.7 Electrical Properties

Resistivity and Sheet Resistivity

The electrical resistivity (R) of a material is given by: $R = \delta L/A$ where δ is the bulk resistivity in ohm-centimeters (Ω-cm), L is the length of the conductor in cm, and A is the crossectional area of the conductor in cm^2. For a square of thin film of thickness (t) and side lengths of (L), the crossectional area becomes $L \times t$ and the resistance from side-to-side of any size square will be the same. This gives rise to the common thin film resistivity unit of ohms/square ($\Omega/\square$) which is called the sheet resistivity (R_s). To obtain the resistivity of the film material in ohm-cm, the film thickness must be known. The resistivity of deposited metals films is generally higher than that of the bulk form of the materials.

The sheet resistance is measured using a linear 4-point probe where the current is injected through the two outer probes and the voltage drop between two inner probes is measured.[73] This avoids problems with contact resistance. A typical commercial unit can measure resistivities

from 1 mΩ/□ to 500 kΩ/□ with a pin pressure of 40–70 grams. The pin separation on the probe of a commercial unit can be as low as low as 0.025 inches. Mercury can be used as a contacting material on the probe tip to avoid damaging pressure-sensitive surfaces.

For a linear arrangement the sheet resistance is given by:

$$R_s = 4.532\ V/I$$

where V is the measured voltage and I is the injected current.

Temperature Coefficient of Resistivity (TCR)

The temperature coefficient of resistance (TCR) of a material is the manner in which the resistance changes with temperature. For metals the TCR is positive (positive TCR)—i.e., the resistance increases with temperature—while for dielectrics, which have a tunneling-type of conduction, the TCR is negative (negative TCR)—i.e., the resistance goes down with temperature. To measure the TCR one only needs to combine a resistance measuring device with a temperature controlled environment.

The TCR of very thin metal films on electrically insulating substrates depends on the growth of the nuclei. Isolated nuclei result in a negative TCR due to the thermally activated tunneling conduction between nuclei. Connected nuclei, which form a continuous film, have a positive TCR as would be expected in a metal. Thus TCR measurements can be used to provide an indication of nucleation density and growth mode by determining the nature of the TCR as a function of the amount of material deposited (Sec. 9.2.2).

Changes of the electrical resistivity of a film having a columnar morphology, may be due to oxidation of the column surfaces. The combination of metallic conduction in the columns and the tunneling conduction through oxide layers on the column surfaces allows the formation of films that have a low, zero, or even negative thermal coefficient of resistivity (TCR) since the effects oppose each other.

Electrical Contacts

Thin film metallization is often used to establish contact with a surface. In many cases, the contact involves reactions which form a layer

of compound material between the metallization and the surface. For instance, in the deposition of platinum on silicon, a layer of platinum silicide is formed. The contact resistance involves not only the resistance between the metallization and the surface but the affect of the reaction layer which can be a high resistivity material or present a potential barrier. In the extreme, the junction may be rectifying (i.e., current can flow in one direction easily but in the other with difficulty). The metallization material can also alloy with the substrate material. For example, gold will diffuse into silicon to some extent and the higher the temperature the higher the solubility of gold in the silicon.

10.5.8 Chemical Stability

Chemical Etch rate

The chemical etch rate of a material by an etchant depends on the solution temperature, surface area (film morphology), residual film stress, film microstructure, stoichiometry, and the solution strength. It also depends on how fast the etch products are removed from the surface and from the vicinity of the surface (i.e. agitation). Gradation of film properties through the thickness can also affect the etch rate. Chemical etch rates are primarily used as a comparative technique.[74] Table 3-11 lists chemical etchants for a number of materials and many more are to be found in the literature.

Corrosion Resistance

Corrosion is an important economic problem and films and coatings are often used to provide corrosion protection. There are a number of corrosion tests.[75] Corrosion resistance in aqueous media (at varying pH) is often measured by weight gain, hydrogen generation (oxidation), or electrochemical corrosion potential.[76][77] One of the most common environmental corrosion tests is the neutral salt fog test. The correlation of the laboratory tests with field failure is often not very good. Thin film metallization corrosion had been studied in HCl environments.[78] Corrosion of thin films may be aggravated by electric fields. Even small amounts of surface material can affect the corrosion of a surface.[79] Accelerated aging for corrosion resistance is often done by increasing the

chemical concentration and/or increasing the temperature. This may be misleading since synergistic effects may be more important.

10.5.9 Barrier Properties

Permeation is the diffusion of a gaseous species (atomic or molecular), (hydrogen, water vapor, oxygen, etc.) into or through a material. Diffusion is the transport of atomic species in a material. The driving force for diffusion and permeation is a chemical concentration gradient or a thermal gradient (thermomigration). When diffusion is from a point source on a surface such as a pinhole in a barrier coating, the diffusion will be both normal to the surface and laterally away from the source.

Diffusion Barriers

Diffusion into and through a material is by bulk diffusion, grain boundary diffusion, and/or surface diffusion in order of increasing diffusion rates. Thin films are often used as diffusion barriers (Sec. 9.7.4). Since in thin films, grain size is typically small compared to bulk materials, the grain boundary mechanism may dominate. However if there is a columnar microstructure then surface diffusion may predominate. Amorphous films seem to be particularly good diffusion barrier materials since they have no grain boundaries.

Diffusion of a molecular species such as hydrogen into a dense solid may involve dissociation of the molecule on the surface, diffusion through the material and re-association on the other surface. In this case, the diffusion rate may be limited by the dissociation and re-association rates which can be changed by adding small amounts of catalytic materials to the surface.

Temperature is an important factor in diffusion and permeation rates. Diffusion is typically a thermally activated process and can be modeled by the Arrhenius equation given by:

$$D = D_o \exp^{(-Q/kT)}$$

where: D_o depends on the diffusion mechanism
Q = activation energy
k = Boltzman constant
T = degrees Kelvin

Permeation Barriers

The units for permeation through a material are weight or volume per unit area per unit time. The oxygen transmission rate (OTR) is determined using *ASTM Standard D 3985-81* and the water vapor transmission rate (WVTR) is measured as per *ASTM Standard F 372-78.* Permeation of gases and water vapor through polymers is of particular interest in the packaging industry.[80] The permeation rate depends on:

- Temperature
- Substrate material (with or without a coating)
- Adsorption of the diffusing material on the surface
- Absorption into the surface
- Solubility in the material
- Diffusivity in the material
- Thickness of the material
- Desorption at the other surface

Aluminum is a common metallizing film material that is used to prevent water vapor or oxygen from permeating through a polymer film material. For example, the OTR for aluminum-metallized polypropylene (PP) can be in the range of 1–10 cc/100cm^2/day. A major problem in measuring the permeation rate through a coated material is the large effect of pinholes, cracks, and microporosity on the measured permeation rate and that the metallized film is often laminated between polymer films to provide mechanical protection. The polymer material generally has a much higher permeation rate than the coating material. Therefore if there is a pinhole or crack that extends through the film, the permeation rate is determined by the area exposed by the pinhole or, if the pore or crack is small, the conductance of the crack/pinhole for the species being measured.

10.5.10 Elemental Composition

The elemental composition of a film can be important to the film properties and is an indication of process reproducibility. In many cases, the elemental composition can change with thickness and some technique must be used that allows depth profiling of the elemental composition. Depth profiling can be accomplished using sputter etching and the surface

spectroscopies of Auger Electron Spectroscopy (AES), Ion Scattering Spectroscopy (ISS), Secondary Ion Mass Spectroscopy (SIMS) and X-ray Photoelectron Spectroscopy (XPS) discussed in Sects. 2.4.1 and 2.4.3. Several techniques are available to non-destructively analyze the elemental composition of a thin film.

X-ray Fluorescence (XRF)

Often it is desirable to non-destructively analyze the film composition without destroying the film. One way of doing this is by X-ray fluorescence (XRF) where the probing species are high energy photons (X-rays) and the detected species are X-ray photons which have specific energies and wavelengths characteristic of the atom adsorbing the radiation.[81]

X-Ray Fluorescence (XRF) is an elemental characterization technique which measures the characteristic X-rays generated when the atoms in a sample are irradiated with X-ray radiation from an X-ray tube or radioactive source. These emitted X-rays are then detected and identified as to their wavelength (Wavelength Dispersive XRF—WDXRF) or energy (Energy Dispersive XRF—EDXRF). The relationship between the wavelength and energy of the radiation is given by:

$$(E_{keV}\, x\, \lambda_{\text{Å}}) = 12.396$$

where E_{keV} is the photon energy in kiloelectron volts and $\lambda_{\text{Å}}$ is the photon wavelength in angstroms.

WDXRF uses diffraction in a crystal spectrometer to determine the wavelength of the radiation and has an energy resolution of about 15 eV. EDXRF uses a lithium-drifted silicon detector to convert the energy of the radiation into an electrical current at a ratio of 3.8 eV of photon energy giving one electron-hole pair. With calibration, the signal intensity provides the amount of material being sampled. Figure 10-6 shows an analytical equipment to utilize both the WDXRF and EDXRF techniques for analyzing a thin film on a wafer-type substrate.

Figure 10-7 shows the relative X-ray fluorescent yields as a function of atomic number. XRF can not analyze elements below an atomic number of nine (9 amu) and has a threshold sensitivity of about 0.1 at%. To obtain quantitative data, the intensities must be calibrated. The calibration is sensitive to the total composition (matrix effect) so the calibration standards must closely approximate the composition of the

sample. Since the X-rays are not easily absorbed, the X-ray emission is detected for an appreciable depth in the solid being analyzed. For example, characteristic X-rays penetrate through a 4000 Å thick tungsten film or a 15,000 Å thick film of aluminum.

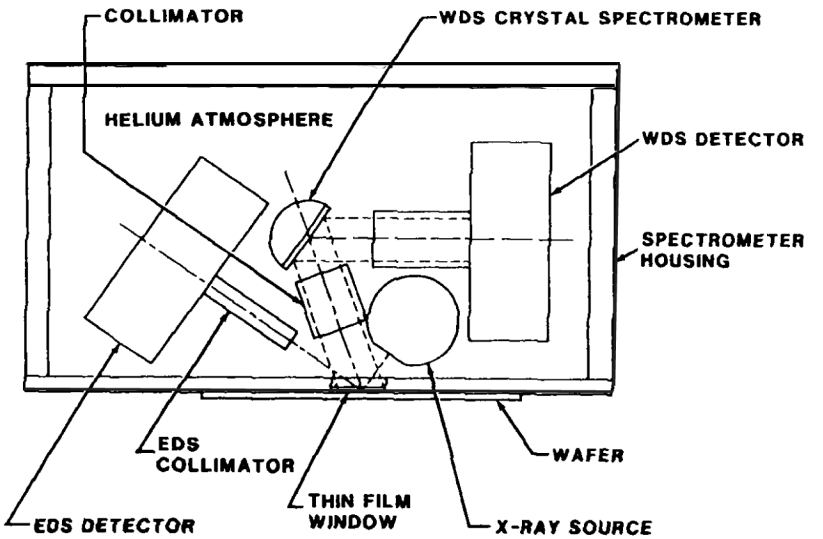


Figure 10-6. XRF apparatus for measuring the intensity, energy and wavelength of emitted X-ray radiation.

The XRF technique is often used in a comparative and non-destructive manner to determine film composition, film thickness, establish the reproducibility of the processing from run-to-run or determine the presence and amount of a critical material or layer. Typical applications of XRF in PVD processing are to analyze the silicon (few percent) and copper (few percent) in aluminum metallization for semiconductor devices, the composition of Ti-W metallization for semiconductor devices, and the titanium, palladium and gold layers in Ti-Pd-Au layered metallization for microelectronics applications. The analysis can be done in air very quickly. The XRF technique measures the number of atoms per unit area sampled but the data can be used for thickness measurement by assuming a film density. Commercial equipment is available.

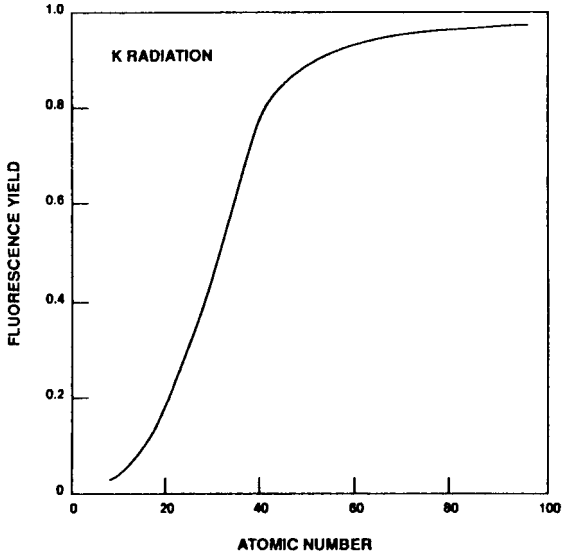


Figure 10-7. Relative X-ray fluorescent yields as a function of atomic number of the sample atoms.

The attenuation of the X-ray signal can also be used to measure film thickness on a substrate by measuring the attenuation (adsorption) of the X-ray signal emitted from the substrate material or by the attenuation of a prominent X-ray signal as it passes through an absorbing film on an X-ray transparent substrate material such as a plastic web. Micro-X-ray fluorescence can be used to study areas as small as 10–100 microns in diameter.

Rutherford Backscatter (RBS) Analysis

Rutherford Backscattering (RBS) is an elemental analysis technique that takes advantage of the energy loss of a high energy penetrating particle when it collides with an atom and is "backscattered" back through the surface of the material.[82][83] Typically a monoenergetic beam of helium ions with energies of several million electron volts (MeV) is used as the probing species. As the MeV ions traverse the solid, they lose energy at a rate of 20–60 eV/Å. The high energy ions are scattered by collisions that involve the Coulombic repulsion between the positively

charged nuclei of the incident and target particles. The probability of collision is given by the differential scattering crossection which is proportional to the square of the charge on the nucleus of the target atom. This crossection is the area that is capable of scattering a particle into a specific angle which is generally near 180° or a direct backscatter along the incident path. For example, for 1 MeV ^{4}He ions, the scattering crossection for scattering at 180° by a target atom (M_{target}) of beryllium (9 amu) is 0.053 x 10^{-24} cm^2/steradian, and for tungsten (184 amu), it is 28.369 x 10^{-24} cm^2/steradian. For comparison, the area subtended by the electronic shell of an atom is about 10^{-15} cm^2. The number that is backscattered is also proportional to the number-density of atoms along the path. For example, fully dense beryllium has an atomic density of 1.2 x 10^{23} atoms/cm^3 and fully dense tungsten has a density of 6.3 x 10^{22} atoms/cm^3.

For direct backscattering (Ø = 180°) of helium ions, the energy ratio between the incident helium ion (E_i) and the scattered helium ion (E_s) is given by:

$$E_s/E_i = (M_{target} - 4)^2/(M_{target} + 4)^2$$

As the backscattered helium traverses the solid it continues to lose energy.

The backscattered helium particles are analyzed as to their number and energy. The number of backscattered particles with a given energy is determined by the number density of the target atoms along the penetration path and the backscatter particle energy is determined by the target-atom mass. Known collision crossection data, atomic number density, and modeling allows this technique to be quantitative without having to use calibration standards. RBS is capable of quantitative analysis with depths to several thousand angstroms, depending on the particle masses, without destroying or modifying the material. It has poor lateral resolution (typically 1 mm diameter beam spot size), poor mass resolution for mixtures of heavy elements, and the surface should be smooth for best resolution. Typically the best depth resolution will be on the order of several hundred angstroms.

RBS can be used to analyze the near-surface region of a solid or can be used to analyze thin films on surfaces. For thin film analysis, RBS is best for a high-z coating on a lower-z substrate as shown in Fig. 10-8. It is also good for detecting a small amount of high-z material in a lower-z matrix, such as boron doping in silicon, but not vice-versa. Figure 10-9

shows the RBS spectra of a thin film consisting of a mixture of equal numbers of silicon, germanium and tungsten and of films of a single material of increasing thicknesses.

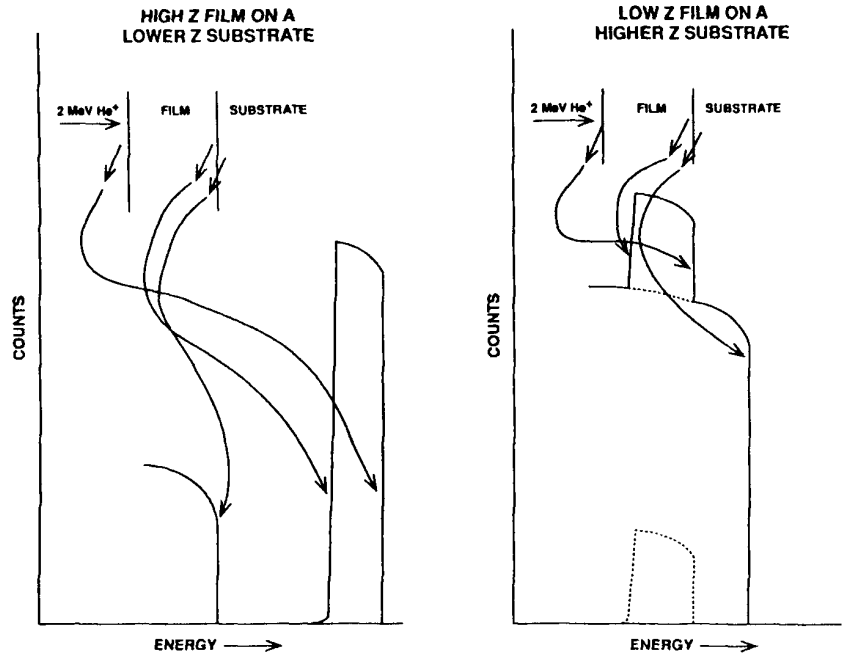


Figure 10-8. The RBS spectra of a high mass film on a low mass substrate and of a low mass film on a high mass substrate. Note the overlapping spectra in the latter case.

RBS is used to establish standards for other analytical techniques such as Auger Spectrometry and for impurity analysis. It can be used to perform "reverse-engineering" on thin film systems to determine the composition and design of an unknown thin film structure. RBS can be used to non-destructively study the diffusion of material at an interface between a film and a substrate as a function of time and temperature. Figure 9-3, shows the RBS profile of a tungsten metallization on a SiGe alloy thermoelectric material before and after high temperature diffusion.

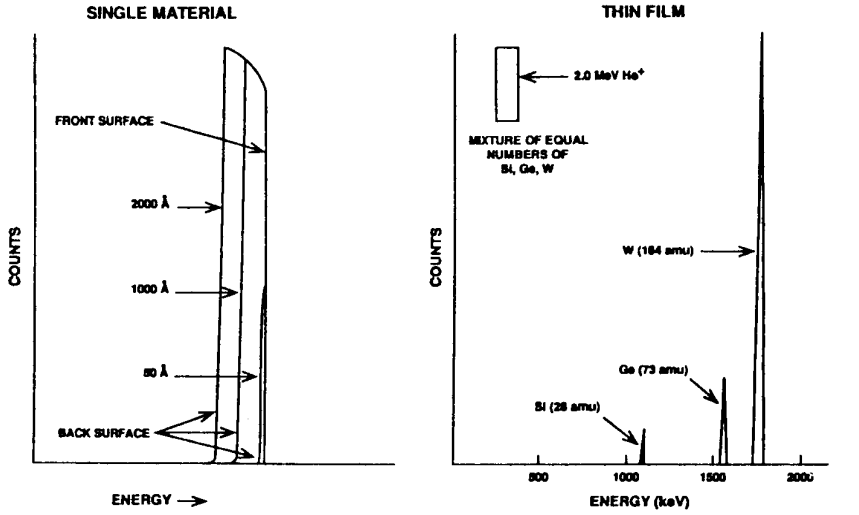


Figure 10-9. The RBS spectra of films of a single material of increasing film thickness and of a thin film consisting of a mixture of equal numbers of silicon, germanium and tungsten atoms.

Electron Probe X-ray Microanalysis (EPMA) and SEM-EDAX

EPMA uses electrons to excite characteristic X-rays which are analyzed for energy or wavelength.[84] Lateral and depth resolution is approximately 1 micron. This technique detects elements with atomic numbers greater than 5 and quantitative analysis may be done on atomic numbers greater than 11. The best analysis is on flat surfaces. Sensitivity is 100 ppm with wavelength-dispersive spectrometry and 1000 ppm with energy dispersive analysis. The technique has poor sensitivity to light elements in a heavy matrix.

The Scanning Electron Microscope can be used for elemental analysis by using the EDAX mode. In the EDAX analytical technique the characteristic X-rays emitted from an electron bombarded surface in the Scanning Electron Microscope are analyzed for their characteristic wavelengths using a crystal spectrometer to give qualitative elemental analysis (X-ray fluorescence). This technique allows both the surface morphology and composition to be determined on the same area.

Solution (Wet Chemical) Analysis

In solution analysis, the material is dissolved in a chemical solution and chemical analysis is performed on the solution[85] or by gas, liquid or ion chromotography.[86] In some cases, very thin surface layers can be preferentially dissolved and analyzed. For example, a thin surface layer can be oxidized and the oxide is preferentially dissolved and analyzed. This technique has been used to profile near-surface compositions to a resolution of 10 Ångstroms.

10.5.11 Crystallography and Texture

Crystallography and crystalline texture (preferred orientation) of thin films is determined using diffraction techniques described in Sec. 2.4.2.

10.5.12 Surface, Bulk and Interface Morphology

The surface morphology of the film can be determined by the techniques of Scanning Electron Microscopy (SEM), Atomic Force Microscopy (AFM) and other techniques described in Sec. 2.4.4.

The bulk morphology of the film is typically determined by fracturing or sectioning the film and the observing the exposed surface by Scanning Electron Microscopy (SEM). The structure can be enhanced by chemical etching. In some cases the film is detached from the surface and thinned to the point that the morphology and crystalininty can be observed by Transmission Electron Microscopy (TEM).

Transmission Electron Microscopy (TEM) and Scanning Transmission Electron Microscopy (STEM)

Transmission Electron Microscopy (TEM) and Scanning Transmission Microscopy (STEM) use the transmission of high energy electrons through a thin sample to image the microstructure of the film.[41][87] The operation of the TEM and STEM differ primarily in the source of electrons. The TEM has a relatively large electron source while the STEM uses a relatively small electron source. STEM instruments are capable of resolutions to the 1 Å range with 2.5–5 Å being more typical.

Sample preparation is often the most difficult part of TEM analysis.[88][89] Not only does the specimen have to be thin but it has to be thinned without introducing damage or artifacts.

Analytical Electron Microscopy (AEM) utilizes a number of electron-probing analytical techniques in the same instrument. One of the principal techniques is STEM or TEM. It also incorporates electron diffraction (Sec. 2.4.2).

10.5.13 Incorporated gas

Gases can be incorporated in surfaces during sputter cleaning and in films during deposition. The gases can be desorbed thermally and measured with a mass spectrometer. The heating can be in stages such that the thermal desorption spectrum can be determined.[90][91] This spectrum can be interpreted as to the binding energy of the gas in the solid structure. The gases can be released by melting or vaporizing the film material.[92]

10.6 SUMMARY

Characterization of the film is an important part of PVD processing, not only because of the functional requirements of the film but also for processing monitoring. Often the first indication that something is wrong with the process is when the properties of the film change. The earlier this can be detected the faster the process problems can be addressed.

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11

Adhesion and Deadhesion

11.1 INTRODUCTION

Cohesion is the strength in a single material due to interatomic or intermolecular forces. Adhesion is the mechanical strength joining two different objects or materials. Adhesion is generally a fundamental requirement of most deposited film/substrate systems. In PVD technology, adhesion occurs on the atomic level between atoms and on the macroscopic level between the substrate surface and the deposited film. The apparent (or practical) adhesion is usually measured by applying an external force to the thin film structure to a level that causes failure between the film and substrate, or in material near the interface (near-by material). This applied force puts energy into the system that causes strain and fracture of chemical bonds. The loss of adhesion is called deadhesion and can occur over a large area to give film delamination from the substrate or over a small area to cause pinholes in the film. Practically, deadhesion can occur at a sharp (abrupt) interface between materials, in an interfacial (interphase) region containing both materials, in the near-interface region of the substrate or in the near-interface region of the deposited film or between films in a layered film structure. Thus, deadhesion can involve both adhesive and cohesive failure. In PVD technology, the adhesion must be good after the film deposition processing, after subsequent processing, and throughout its service life. This requires that the evaluation of the

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adhesion involves an adhesion test program that subjects the film structure to all of the factors that may degrade the adhesion. These include: mechanical, chemical, electrochemical, thermal, and various types of fatigue involving extended times.

11.2 ORIGIN OF ADHESION AND ADHESION FAILURE (DEADHESION)

The adhesion of a film to a surface involves adhesion on the atomic scale as well as the failure of the atomic bonding over an appreciable area on a macroscopic scale.

11.2.1 Chemical Bonding

Ionic bonding occurs when one atom loses an electron and the other gains an electron to give strong coulombic attraction. Covalent bonding occurs when two atoms share two electrons. In ionic and covalent bonding, there are few "free electrons" so the electrical conductivity of the material is low and the material is brittle. Polar covalent bonding occurs when two atoms share two electrons but the electrons are closer to one atom than the other, giving a polarization to the atom-pair. Metallic bonding is when the atoms are immersed in a "sea" of electrons which provides the bonding. Metallically bonded materials have good electrical conductivity and the material is ductile. In some materials there is a mixture of bond types. Van der Waals or dispersion bonding occurs between non-molecules when a fluctuating dipole in one molecule induces a dipole in the other molecule and the dipoles interact producing bonding. The surface of solid polymers consists of a homologous mixture of dispersion and polar components in differing amounts for the various polymers. For example, polyethylene and polypropylene surfaces have no polar component only dispersion bonding.

11.2.2 Mechanical Bonding

Adhesion by mechanical means can occur by mechanically interlocking ("keying") the two surfaces such that one material or the other

must deform or fracture for the materials to be separated. This type of bonding requires that the deposited film be conformal to a rough surface and that there are no voids or poorly contacting areas at the interface.[1]

11.2.3 Stress, Deformation, and Failure

Tensile stress is when the mechanical stress is applied normal to and away from the interface. Shear stress is when the mechanical stress is applied parallel to the interface. Compressive stress is when the mechanical stress is applied normal to and toward the interface. When a tensile stress is applied to the surface of a film, the stress that appears at the interface between dissimilar materials, will be a complex tensor with both tensile and shear components whose magnitudes will depend on the applied stress and the mechanical properties of the materials. For example, the stress tensor will be different for a metal film on a polymer (low modulus of elasticity) substrate and a metal film on an oxide (high modulus) substrate. The nature of the film failure will differ depending on the relative properties of the film and substrate. For example, a high modulus film, such as an oxide, on a substrate that can elongate or deform easily can have good adhesion but the film can crack under stress.[2]–[6] This is an important failure mode for oxide coatings on flexible materials used for food packaging where the goal is to prevent water vapor from penetrating through the film.

Deformation of a material requires the input of energy and the deformation can be elastic, plastic or a mixture of the two. This deformation may occur over a large volume of material or just at the tip of a propagating crack. Elastic deformation is when the applied stress causes deformation (elongation or strain) but when the force is removed the material returns to its initial dimensions. Young's Modulus of Elasticity is the ratio of the stress to the strain in the elastic deformation region. If a rod of material is subjected to a uniaxial tensile stress, it will elongate and the crossectional area will decrease. Poisson's ratio is the ratio of the transverse contracting strain to the axial elongation strain. Plastic deformation is when the applied stress causes a permanent deformation of the material. The yield stress is the stress level at which the material begins to exhibit plastic (permanent) deformation. At some level of deformation the material will fail. The amount of energy that must be put into the system to cause this failure is a measure the fracture toughness of the system and is a measure of the cohesive or adhesive strength.

11.2.4 Fracture and Fracture Toughness

The loss of adhesion under mechanical stress occurs by deformation and fracture of material at or near the interface.[7]–[9] When a fracture surface (crack) advances, energy is needed for the creation of new surfaces and deformation processes that occur around the crack tip. This energy is supplied by the applied stress and the internal strain energy stored in the film-substrate system (residual film stress). The path of crack propagation is determined by the mechanical properties of the materials and by the resolved tensor stresses on the crack tip. The crack may progress through weak material or may be diverted into stronger materials by the resolved stress. The fracture path depends on the applied tensor stress, the presence of flaws, the interface configuration, "easy fracture paths", and the properties of the materials involved. The fracture path is also determined by the presence of features which may blunt or change the fracture propagation direction.[10] The fracture may be brittle (brittle fracture), with little energy needed to propagate the crack, or ductile (ductile fracture) where there is appreciable plastic deformation before failure and much more energy is needed to propagate a crack. The fracture mode (brittle or ductile) depends on the properties of the materials.

The fracture toughness (K_c) of a material is a measure of the energy necessary for fracture propagation and is thus an important adhesion parameter. In fracture, energy is adsorbed in the material and at the propagating crack tip, by elastic deformation, plastic deformation, generation of defects, phase changes and the generation of new surfaces. If this fracture occurs at an interface or in the near-by material, then loss of adhesion (deadhesion) occurs. Fracture mechanics approaches to measuring, describing, modeling, and/or predicting thin film (or any interface) adhesion are few. Thouless has described the problem of critical and subcritical crack growth in thin film systems.[11] Some work has been published on the fracture of thick film[12]–[16] and thin film[17]–[19] systems. Very little has been done to elucidate the effects of environment (subcritical crack growth[17] and film properties[20][21] on fracture and adhesion of thin film systems.

The fracture toughness of a material depends on the material composition, the microstructure, the flaw concentration, and the nature of the applied stresses. If an interphase material has been formed in the interfacial region, it will be involved in the fracture process. Such interphase material is formed by diffusion, diffusion plus compound

formation, and by physical processes such as mixing during deposition or recoil implantation (Sec. 9.3). The interphase material may be weaker or stronger than the nearby film and/or substrate material. For example, carbon lost from high carbon steel substrates by diffusion into the film material during high temperature processing may weaken the substrate and strengthen the film material near the interface.[22]–[24]

The fracture of a brittle material is often accompanied by acoustic emission which results from the release of energy.[25][26] This acoustic emission has both an energy and a frequency spectrum.[27][28] Acoustic emission can be used as one indication of the onset of failure. For example, in the testing of adhesion by the scratch test, the coated surface is scratched by a rounded diamond point and the load on the point is increased while monitoring the acoustic emission using a piezoelectric accelerometer to detect the onset of fracture (Sec. 11.5.2).

In the thermal-wave testing of material, a thermal pulse is introduced into the solid and where there is a discontinuity in the material (interface, defect, etc.) a stress is generated. If this stress gives rise to acoustic emission, this emission can be detected and an image of the discontinuity can be made. The thermal wave technique can be used to detect subsurface flaws in the material. The Scanning Laser Acoustic Microscope (SLAM) is an analytical technique based on this effect.

The fracture of a brittle, electrically insulating material is often accompanied by the emission of electron, photon and/or ions. This "fractoemission" is probably due to microarc discharges resulting from charge separation during fracture.[29]–[31]

11.2.5 Liquid Adhesion

The generation of the interface in liquid-solid contact and the mechanism of adhesion are quite different from that formed in thin film deposition, but some basics of this system may be of interest. In liquid adhesion, typically one component is a fluid that is applied to a solid surface where it wets and spreads over the surface giving intimate contact. When the fluid solidifies, there is adhesion between the coating and the surface with a miniminal amount of residual stress in the interface and good interfacial contact. The properties of the adhesive interface will depend on the functional groups present on the surface and will depend the vapor contacting the surface. For example, the fluid surface properties may be different if the surface has been in an inert atmosphere (argon,

nitrogen) or in a water vapor-containing atmosphere.[32][33] The adhesion properties of liquid films on surfaces is of interest in microelectronics industry.[34]

Surface Energy

The surface energy results from non-symmetric bonding of the surface atoms/molecules in contact with a vapor and is measured as energy per unit area (Sec. 2.4.6).[35] Basically, if there is no elastic or plastic strain, the surface energy is about one-half of the energy needed to create two new surfaces in the fracture of a solid. Solids strive to minimize their surface energy by reaction or adsorption.

Acidic-Basic Surfaces

An atom or a surface can be acidic or basic in nature. An acid is an electron acceptor while a base is an electron donor. The degree of acidity or basity is dependent on the materials in contact. An acidic surface will react with a basic atom while a basic surface will react with an acidic atom. The electronic nature of a surface can be changed by changing the chemical composition. Polymer surfaces can be acidic or basic in nature.[36] Polymer surface treatments, such as oxygen plasma treatments, make the polymer surface more acidic and thus able to react with many metallic atoms. An amphoteric material is one that can act as either an acid or a base in a chemical reaction. Aluminum is an example of an amphoteric material and shows good adhesion to both acidic and basic polymer surfaces.

Wetting and Spreading

Wetting of a surface by a fluid is controlled by the Young Equation (Eq. 11-1), which relates the equilibrium contact angle (θ) of the fluid (Fig. 2.12) to the interfacial tensions (γ) between the liquid and vapor (*LV*), the solid and the vapor (*SV*) and the solid and the liquid (*SL*).

Eq. (11-1) $$\gamma_{LV} \cos\theta = \gamma_{SV} - \gamma_{SL}$$

The rate of spreading of a fluid over a surface depends on the surface morphology, fluid viscosity and the Young relationship. For

example, roughening a surface increases the spreading rate due to capillary effects and lowering the fluid viscosity increases the spreading rate.

Work of Adhesion

The thermodynamic adhesion (work of adhesion—W_a) between two polymer materials (1 and 2), in ideal contact, is given by the Dupre relation:

$$W_a = \gamma_1 + \gamma_2 - \gamma_{1,2}$$

where γ_1 and γ_2 are the surface energies and $\gamma_{1,2}$ is the interfacial energy. The highest adhesion is between surfaces having opposite polarity (acid-base) and high surface energies.[37]–[40] There are a number of techniques to change the acid-base nature of surfaces and to increase the surface energy of the polymer surface. "Coupling agents" or primers, which bond to each surface by a different mechanism, can be used to decrease the interfacial energy between the polymers.

11.3 ADHESION OF ATOMISTICALLY DEPOSITIED INORGANIC FILMS

Good adhesion requires strong chemical bonding between dissimilar atoms, intimate contact between the dissimilar materials, a high fracture toughness of the materials in contact, low residual stress in the interfacial region, and no degradation mechanism operating. Even if the chemical bonding involves a weak bond such as the van der Waals bond, the adhesion can still be good if the dissimilar atoms are in good atomic contact. The properties of the interface and interfacial material are important to the adhesion. The interface, interfacial material, and nearby material should have a high fracture toughness and no flaws that act as stress concentrators and initiate cracks under stress. The deposition process itself can affect adhesion particularly if concurrent ion bombardment (ion plating) is used.[41]

11.3.1 Condensation and Nucleation

Condensation of atoms on a surface releases energy that affects the surface mobility of the adatoms and chemical reactions on the surface (Sec. 9.2). The surface mobility and chemical reactions affect the nucleation of the adatoms on the surface.

Nucleation Density

The nucleation density of the deposited atoms is an early indication of good or poor contact. A high nucleation density indicates strong chemical interaction of the deposited adatoms with the substrate surface and is desirable for good adhesion. A low nucleation density indicates poor interaction and the development of poor interfacial contact and the formation of interfacial flaws which will lead to poor adhesion.

11.3.2 Interfacial Properties that Affect Adhesion

11.3.3 Types of Interfaces

In PVD processing, the depositing film material nucleate on the surface and react with the substrate to form an "interfacial region" (Sec. 9.3). The material in the interfacial region is called the "interphase material" and its properties are important to the adhesion in film-substrate systems. The type and extent of the interfacial region can change as the deposition process proceeds or be modified by post-deposition treatments, storage or service. Interfacial regions are categorized as:

- Abrupt
- Mechanical (a type of the abrupt interface)
- Diffusion
- Compound (also requires diffusion)
- Pseudodiffusion (physical mixing, implantation, recoil implantation)
- Graded
- Combinations of the above

Figure 9-2 schematically shows the types of interfacial regions. Roughening the substrate surface can improve or degrade the adhesion depending on the ability of the deposition technique to fill-in the surface roughness and the film morphology that is generated.

11.3.4 Interphase (Interfacial) Material

The nature of the interfacial material is important to developing a fracture-resistant interfacial material. A diffusion-type or compound-type interfacial region is good for adhesion provided excessive diffusion and reaction does not introduce voids, stresses and fractures in the interfacial region. A DOE -BES Workshop in 1987 determined that the properties of the "interphase" (interfacial) material is one of the critical concerns in quantifying, measuring, and modeling the adhesion failure process[42] and the situation has not changed. At present there are few, if any, good characterization techniques for determining the properties of interfacial materials such as fracture toughness, deformation properties, interfacial stress, presence of microscopic flaws, or effects of degradation mechanisms. Usually, observation of the failed surface is the best indicator of the failure mode.

The energy necessary for fracture propagation (fracture energy) may be lessened by mechanisms that weaken the material at the crack tip or reduce the elastic-plastic deformation in the vicinity of the crack tip. These mechanisms may be dependent on the environment such as moisture[43] or hydrogen in the case of ionically bonded materials.[44] If time is involved in reducing the strength of the crack tip, the loss of strength is called "static fatigue." Static fatigue depends strongly on mechanical (stress) and environmental (chemical) effects, particularly moisture.[45]

Brittle surfaces and interfaces can be strengthened by placing them in compressive stress.[46][47] This can be done by stuffing the surface with larger ions (chemical strengthening), ion implantation, or by putting the bulk of the interior material into tensile stress (Sec. 2.6.3). The surfaces can also be strengthened by removing surface flaws such as cracks introduced by grinding.

If the film-substrate interface is smooth, then any interfacial growth defects, such as interfacial voids, will lie in a plane which will then be an "easy fracture path" or "plane-of-weakness" along which fracture will easily propagate. If the surface is rough and the deposited film material "fills-in" the roughness, the propagating fracture must take a

circuitous path with the likelihood that the fracture will be arrested and have to be re-initiated as in the case of composite materials.[10] If the roughness is not "filled-in," then there will be weakness (voids and low contact area) built into the interfacial region. Therefore the nature of the substrate surface roughness and the ability of the deposition process to fill-in this roughness is important to the development of good adhesion.

11.3.5 Film Properties that Affect Adhesion

Many film properties are important to the apparent adhesion and adhesion failure.

Residual Film Stress

An important factor in the apparent adhesion is the residual film stress (Sec. 10.5.1). Invariably, PVD films have a residual stress which can be either tensile or compressive and can approach the yield or fracture strength of the materials involved. These stresses arise from differences in the thermal coefficient of expansion between the film and substrate in high temperature depositions, thermal gradients established in the depositing film, and stresses due to the growth processes. The total stress that appears at the interface from residual film stress will depend on the film thickness and the film material. High modulus materials such as chromium, tungsten, and compound materials generate the highest stresses. These stresses will be added to any applied stress, decreasing the measured apparent adhesion,[48] and can be capable of causing spontaneous deadhesion of the film. Residual film stress can also accelerate corrosion processes.

Film Morphology, Density and Mechanical Properties

Film properties can influence the apparent adhesion of a film-substrate couple (Sec. 10.5.4, 10.5.6). The deformation, microstructural, and morphological properties of the film material determine the ability of the material to transmit mechanical stress and to sustain internal stresses. For example, a film with columnar morphology may exhibit good adhesion because each column is separately bonded to the substrate and the columns are poorly bonded to each other.[21] In other cases, the apparent adhesion of a film may be decreased by the columnar morphology.[49][50]

The columnar morphology is generally not desirable because of its porosity which allows easy interfacial corrosion and allows the adsorption and retention of contaminants that can contribute to corrosion.

The mechanical properties of the film determine the stress distribution that appears at the interface. In cases where there is a large difference in the physical and mechanical properties of the film and substrate, it may be advantageous to grade the properties through the interfacial region rather than have a sharp discontinuity in properties. For example, in the coating of tool steel with TiN it may be desirable to first deposit a thin layer of titanium on the steel and then grade the Ti-N composition gradually to the stoichiometric composition TiN. This can be done by controlling the nitrogen availability in the plasma during deposition. The same procedure is used in growing single crystal SiC layers on silicon.[51]

Flaws

Flaws at or near the interface are often the determining factor in adhesion. Flaw initiation generally takes more energy than flaw propagation and the presence of preexisting flaws decreases the fracture toughness of the material. The flaws can also concentrate the stress making the local stresses high. Flaws at the interface can be present from flaws in the substrate surface, incomplete contact of the film with the substrate, or growth effects such as voids. Flaws can be generated by the deposition of highly stressed thin films. For example, if the film has a high compressive stress it will place the substrate surface in a tensile stress that can produce flaws.[52]

Lattice Defects and Gas Incorporation

Lattice defects and mobile gaseous species that are incorporated into the growing film can coalesce into voids. Boundaries between dissimilar materials, such as grain boundaries, interfaces and surfaces, are preferential sites for these voids to form. When they form at an interface, they provide a “plane-of-weakness” that weakens the interfacial region allowing loss of adhesion. This can be a problem when the substrate surface has been “charged” with hydrogen during acid cleaning or by gas during sputter cleaning.

Pinholes and Porosity

Pinholes and through-porosity (Secs. 9.4.2 and 10.5.4) allow easy access to the interface by corrosive agents. Process parameters that affect the growth of the columnar microstructure affects the films porosity. For example, the porosity of vacuum deposited films can be varied by controlling the substrate surface roughness or angle-of-incidence of the adatom flux.[53]

Nodules

Nodules in deposited films can be formed by growth discontinuities on surface features such as particulates or by molten droplets ("spits" or "macros") from the vaporization source.[54] The particulates or spits can be on the substrate surface initially or can be deposited on the film surface during film growth. Nodules are generally poorly bonded to the surface and can easily be dislodged to give pinholes.

11.3.6 Substrate Properties that Affect Adhesion

In Ch. 2 the nature of "real" surfaces and the associated substrate material was discussed. In order to have good adhesion it is important that the substrate surface and near-surface material have a high fracture toughness.* It is important that the surface not contain flaws that become part of the interfacial region since these flaws will weaken the interfacial region. The permeation/diffusion barrier properties of the substrate material may be important. For example, one mode of failure of aluminum metallized plastic film is diffusion of water from the un-metallized side of the polymer surface.

Gases can be included into the substrate surface during surface preparation processes such as acid cleaning or *in situ* sputter cleaning.

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*The problem was adhesion of metallization to ferrite components. One supplier provided adherent metallization, another did not. The assumption was that there was something different in the metallization process. The problem turned out to be that the surface of the ferrite prepared by one manufacture was friable while that used by the other was dense and hard. The adhesion failure was in the friable ferrite surface not at the interface between the film and the surface. The difference in fracture properties of the ferrite was evident when the surfaces of the two ferrite materials were scraped with a knife-point.

After the film has been deposited. these gases may accumulate at the interface giving poor film adhesion.

11.3.7 Post-Deposition Changes that Can Improve Adhesion

In some cases, the apparent adhesion of a film to a surface increases with time after deposition.[55]–[57] This may be due to the diffusion of a reactive species such as oxygen to the interface or by stress-relief of the film with time.[58] For instance, plasma cleaning of glass surfaces prior to silver deposition has been shown to give a time dependent improvement in the adhesion of the silver films after deposition.[59] This effect is usually noted when the adhesion is not very good in the first place.

An example of the interface changing with time is shown in the chromium metallization of glass. The chromium will react with the glass to form chromium oxide, which is an electrical conductor. The amount of chromium oxide determines the amount of interfacial material present. If the chromium is removed immediately after deposition, it is found that the resistivity of the oxide layer is less than if it removed after the metallization has been "aged" at ambient conditions for months or years. This indicates that the interfacial reaction proceeds slowly after deposition even at ambient temperatures.

11.3.8 Post-Deposition Processing to Improve Adhesion

Ion Implantation

Postdeposition treatment by high energy (MeV) ion bombardment (implantation) where the bombarding particle passes through the interfacial region, has been reported to increase film adhesion.[60]–[74] The process has been called recoil mixing, ballistic mixing, and interface "stitching." If the materials involved are miscible, the ion mixing results in interfacial reaction and diffusion, however if the materials are immiscible the interfacial region is not mixed but the adhesion may be increased. Even where there is no interfacial diffusion, the penetrating ions may eliminate interfacial voids by "forward sputtering" material from the top of the void to the substrate surface which would increase the adhesion. Generally there is a dose dependence on adhesion improvement with the best result being

for doses of 10^{15}–10^{17} ions per cm^2. The ion bombardment and energy release may also anneal the film[75] and reduce the residual stress.

Heating

Postdeposition heating can increase film adhesion by stress relief of the residual film stresses (annealing)[76] or by increasing interfacial diffusion and reaction. However heating must be used with care since it often can cause strength degradation by affecting the interface and interfacial material. The composition of the gaseous ambient can affect the diffusion process.[77] Heating can also cause agglomeration of the film material on the surface.[78]

Mechanical Deformation

Mechanically burnishing or shot peening the surface of a soft film (Sec. 9.6.3) can close pinholes and decrease the possibility of interfacial corrosion that can cause failure. Shot peening also introduces compressive stress into the film.

11.3.9 Deliberately Non-Adherent Interfaces

In some situations adhesion is not desirable. For example one technique for forming free-standing films, foils or shapes is to deposit a coating on a mandrel and then separate the coating from the mandrel. The coating may be deposited on a substrate to which it will not adhere or a "parting layer" (release layer) can be used.[79] Coating onto a moving surface and then peeling the deposit from the surface is used to make beryllium[80] and titanium alloy foil.[81]

11.4 ADHESION FAILURE (DEADHESION)

Loss of adhesion at the interface, in the interfacial (interphase) material, or in near-by material can occur due to a number of effects. These include: mechanical stress, chemical corrosion, diffusion of material to or away from the interface, or fatigue effects. Sometimes several

factors are involved at the same time such as stress and corrosion. In some cases, film properties influence the failure mechanism. For example, residual film stress can add to the applied mechanical stress and can even stress the interface to such an extent that adhesion failure occurs without any externally applied stress.

11.4.1 Spontaneous Failure

Film adhesion may fail spontaneously without the application of any stress. This can be due to very poor adhesion or to high residual film stress.[48] High residual compressive stress can cause blistering of the film from the surface, as shown in Fig. 11-1.[82] A high tensile stress can cause microcracking and flaking as shown in Fig. 11-2. If the compressive stresses are isotropic, the blistering will be in the form of "wormtracks." If the tensile stresses are isotropic, the microcracking will be in the form of a "dried-mudflat" cracking pattern often with the edges curled away from the substrate as shown in Fig. 11-3. If the film adhesion is high or the fracture strength of the surface is low, the actual fracture path may be in the substrate and not at the interface. The residual stress that can be attained depends on the elastic modulus of the film material. A soft material will not sustain a high stress, it will deform. The elastic modulus of soft materials can be increased by gas incorporation during deposition.[83] The film stress can vary through the thickness of the film. This film stress profile leads to "curling" of a film when it is detached from the substrate.[84] If the adhesion failure is such that some of the substrate material remains attached to the film, the film can curl because of the constrained surface.

Localized regions of high intrinsic stress may be found in films due to growth discontinuities. Local stresses can be found in films where there is non-homogeneous growth such as around steps and defects in the film. These stressed areas can lead to localized adhesion failure giving pinholes (pinhole flaking).

If high residual film stresses are being generated during deposition, they can often be limited by restricting the film thickness, changing the film materials, changing the film structure, or by changing the deposition technique or deposition parameters.[85] For example, when depositing an electrically conductive layer of chromium on glass it is often found that when the chromium thickness exceeds several thousand Ångstroms the residual film stress will peel-up a layer of the glass. To avoid the problem, the chromium thickness can be limited to less than 500 Ångstroms and the

desired electrical conductivity obtained using a top layer of gold or copper which does not develop high stresses since the yield stress is low. If this is not done, the stress in the thick deposited chromium films must be carefully controlled. Another commonly encountered problem is the high compressive stresses that can be developed in low-pressure sputter deposition where high energy reflected neutrals from the sputtering target bombard the growing film. The compressive stresses can be lowered by increasing the deposition pressure so as to "thermalize" the high energy reflected neutrals before they reach the growing film surface.[86]

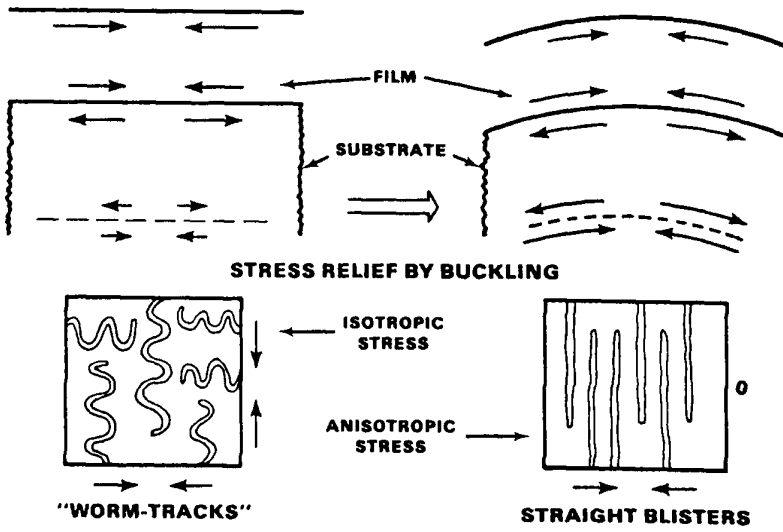


Figure 11-1. Compressive film stress.

11.4.2 Externally Applied Mechanical Stress—Tensile and Shear

When an external tensile stress is applied to the surface of a film, it will appear at the interface as a tensor force with both tensile and shear components. The components of the stress will depend on the mechanical properties of the film and substrate materials.[87] If the substrate is rigid, the more ductile the film material, then the higher is the shear component. If a compressive stress is applied to the surface, the shear component will

be high. If the substrate deforms under load, the stress tensor will be further complicated. Often the mechanical properties of the film material are unknown. Modeling the stress tensor at the interface is difficult if not impossible.

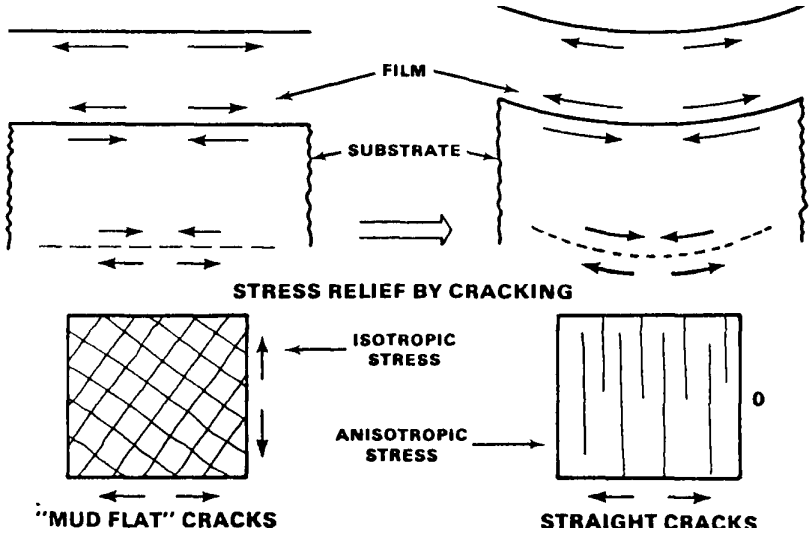


Figure 11-2. Tensile film stress.

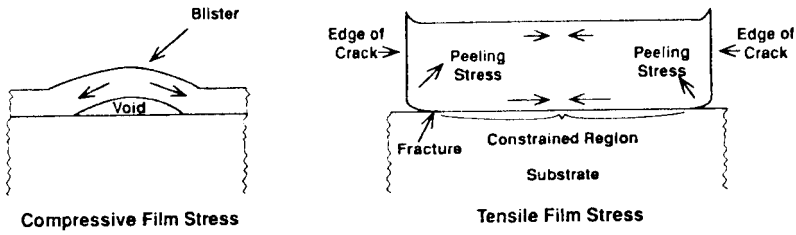


Figure 11-3. Blistering of a film from the surface leaving a void. Microcracking and peeling of a "flake" from a surface.

11.4.3 Chemical and Galvanic (Electrochemical) Corrosion

Chemical corrosion is the chemical reaction of materials at the interface to form a compound. The compound that is formed often has poor mechanical strength and, in addition, there is usually a volume expansion when the compound is formed. In corrosion at an interface, it is often found that solid or gaseous corrosion products expand creating a "wedging action."[88] Corrosion may be present due to subsequent processing, such as in chemical etching, or may be present from contaminant sources such as degraded chlorine-containing solvents which have not been removed or chemicals in the atmosphere from cleaning, etching or other sources. Often "interfacial corrosion" proceeds at a rapid rate and is often undetected until large areas of the film comes off. The stress around the wedge enhances the corrosion rate. Tensile stress at the crack-tip enhances the corrosion rate (stress corrosion). Therefore residual film stress can play an important role in interfacial corrosion.

Often interfacial corrosion initiates from pinholes in the film. Interfacial corrosion can also be due to reactive species trapped at the interface, migration down through-porosity, permeation or diffusion through the substrate, or permeation or diffusion through the film material. Surface corrosion of films can sometimes be reduced by formation of a passive layer or deposition of an inert film. For example, a thin film of gold ("flash") is often deposited on the surface of a copper metallization to prevent surface corrosion.

Electrochemical (or galvanic) corrosion is the dissolution of material under an electrical potential in the presence of an electrolyte. The potential can be externally supplied or be due to the difference in electromotive potential between two materials (Table1-2). For example, in the case of Ti-Au metallization a galvanic couple can be established that corrodes the interface resulting in the loss of adhesion.[89] This electrochemical degradation can be prevented by the addition of a thin intermediate layer of palladium or platinum between the titanium and the gold. The chloride ions to form the electrolyte, are often present as residues from cleaning and processing steps.[90] In another example, the presence of the Al_2Cu nuclei in a Al-2%Cu aluminum metallization form a galvanic corrosion couple and corrosion pitting can occur if there is an electrolyte present.[91][92] The Al_2Cu acts as a cathode (-0.73 volts) while the Al acts as the anode (-0.85 volts).

11.4.4 Diffusion to the Interface

Interfaces generally will act as preferential condensation regions for diffusing species. Diffusion of species to the interface can weaken the interface. Precipitation of gas, incorporated into the film during deposition or in the substrate surface during cleaning, at the interface will reduce adhesion by forming voids at the interface. The diffusion of hydrogen through a film to an interface where it precipitates has been used by the electroplating community as an adhesion test.[93] Diffusion and precipitation of lattice defects also forms voids at interfaces which causes adhesion loss.

Diffusion of water vapor through a polymer film to the interface can lead to the degradation of metal-polymer adhesion.[94] Interfacial mixing can improve the moisture degradation properties of polymer-metal film systems.[95]

11.4.5 Diffusion Away from the Interface

Diffusion away from the interface can cause loss of adhesion. For example, in the chromium-gold metallization, heating in air above 200°C will cause the chromium to diffuse from the interface to the gold surface where it will oxidize. The formation of this chromium oxide surface layer hinders thermocompression bonding of wire leads to the surface and the loss of chromium from the interface leaves voids and decreases the adhesion.[96] This out-diffusion of the interfacial material is dependent on the gaseous ambient and a non-oxidizing ambient reduces the diffusion.

11.4.6 Reaction at the Interface

As discussed in Sec. 9.3, the material that forms the interfacial region can be weakened by voids and microfracturing, especially if the interfacial region is extensive. The extent of the interfacial region depends on the materials involved, the temperature, and the time.

For example, in the Au-Al metallization system, prolonged exposure to a temperature above 200°C in service will cause progressive interfacial diffusion and reaction which forms both Kirkendall voids and a brittle purple-colored intermetallic phase ($AuAl_2$) termed "purple plague" which contains fractures due to the volume expansion on forming the new phase. These effects weaken the interface and cause failure with time.[97][98] Examination of the fractured surface after failure shows the purple color of the $AuAl_2$ and the roughness caused by the formation of the voids.

11.4.7 Fatigue Processes

Fatigue is the cyclic application of a stress. The stress may be thermal, chemical, or mechanical. The effects of the cyclic stress can lead to failure even though one application of the stress does not. Fatigue failure can be due to the generation of flaws, progressive extension of a crack (sub-critical crack growth) or by changes in the mechanical properties of the materials (e.g. workhardening). For example, the cyclic application of a temperature to the surface of a TiC film on copper ultimately leads to loss of adhesion because of the void generation at the interface due to the differences in coefficient of thermal expansion of materials on either side of the interface (ratcheting effect).[99][100]

Static fatigue is the slow growth of a crack under ambient stress and environmental conditions.[43][45] The static fatigue failure in oxide materials can be accelerated by moisture or hydrogen[44] which weakens the chemical bonds at the crack tip. This moisture can be supplied by breathing on the films to condense moisture. This moisture condensation method is an easy method of quickly determining if the residual film stresses are high, the adhesion is poor, and the nature (compressive or tensile stress) of the stresses in a film. This moisture condensation is the basis of the "bad breath" adhesion test (Sec. 11.5.2).

11.4.8 Subsequent Processing

Postdeposition processing and service may weaken the interfacial region by introducing flaws. An example is the heating of a system where the film and substrate have different coefficient of expansions thus stressing the interface during thermal cycling and initiating flaws.* Stressing the film-substrate system may result in cracking the substrate or

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*An ex-student called up with the following problem. They deposited a thick tungsten layer (2000 Å) on glass and the adhesion was good. They then had a high-temperature processing step after which the measured adhesion was good. They then had a diamond saw slicing operation during which the film fell off. The question was "what is going on?" I proposed the following scenario. During heating, the thick tungsten film stressed the interface, due to coefficient of expansion mismatch, and this produced flaws just like scratching a piece of glass. These flaws did not propagate. During diamond sawing, when water was able to reduce the strength of the crack tip, the flaws were able to propagate. (Just like wetting a scratch when you scribe glass to break it.) The proposed solution to the problem was to use a thinner tungsten film which would apply less stress on the interface during heating. The proposed solution worked.

the film.[4][5] These fractures may then be the initiation points for fracture in the interface as well as cause degradation of other film properties. For example, film fracturing is a problem when depositing a brittle film, such as SiO_2, on a flexible web for use as a transparent permeation barrier coating.

11.4.9 Storage and In-Service

Improper storage can degrade the adhesion. For example, the film may be stored by wrapping in a polymer containing chlorine and moisture. Corrosion then attacks the film and the interface. Time itself can cause failure. For example, an encapsulated aluminum conductor-stripe that has a high tensile stress will generate voids and cause separation at the grain boundaries (Sec. 9.6.6).[101]–[103]

11.4.10 Local Adhesion Failure—Pinhole Formation

Pinholes in films can be formed by local regions having poor adhesion usually due to particulate contamination. The pinholes are revealed by stresses that remove the film in the form of flakes (pinhole flaking). These stresses can be mechanical such as wiping, or thermal such as a laser pulse.

11.5 ADHESION TESTING

Adhesion testing is used to monitor process and product reproducibility as well as for product acceptance. The objective of adhesion testing is to duplicate the stresses and associated times to which the interface will be subjected during fabrication and in service. This may be difficult to do in practice.[8][104] Adhesion testing can be done at several stages of the processing in order to identify processes that may degrade adhesion. Adhesion tests are generally very difficult to analyze analytically and are most often used as comparative tests.

Typically adhesion testing is done by lot sampling on product or witness samples that are representative of the product. It should be remembered that the properties of the substrate material and surface preparation procedures may have an important effect on the measured adhesion so the

witness sample material and its preparation should be representative of the product processing. For example, the product surface may be curved and a witness sample with a flat surface is prepared using the same material, surface finish, surface preparation, and deposition process so that a stud-pull adhesion test can be used. Stressing a film to test for adhesion can result in degradation such as cracking the film, can contaminate the film, or can weaken the interface or substrate. Care must be taken if the tested surface is to be subsequently used as product.

Often the adhesion test methods involve testing over an appreciable area. Do not neglect local effects. For example, the tape test not only evaluates overall adhesion but observation of the tape can show "pull-outs" where there is local failure that produces pinholes in the film.

11.5.1 Adhesion Test Program

Adhesion testing should evaluate the coating under stresses similar to those encountered in subsequent processing, storage, and service not just the adhesion after film deposition. The test program should also subject the coating to environmental stress (time, temperature, chemical, mechanical fatigue, etc.) in order to evaluate the stability of the adhesion in the service environment.

11.5.2 Adhesion Tests

Adhesion tests are generally used to provide comparative measurements and are not meant to give any absolute measurement. In many cases, different tests will give different values and even show a different failure mode.[105] There are hundreds, if not thousands, of adhesion tests and test variations.[100]–[108] The use of acoustic emission with some adhesion tests can give an indication of the onset of failure but generally total failure is what is measured. The best test of adhesion is functionality under processing, storage and service conditions!!!!

Adhesion tests may be divided into the method that stress is applied to the film/coating. Adhesion test methods include: tensile tests, peel tests, shear tests, deformation tests, energy-deposition tests, fatigue (thermal, mechanical) tests and many others. Some of these tests are depicted in Fig. 11-4. Adhesion testing of thin films on flexible substrates such as webs is a particularly difficult problem.[109]

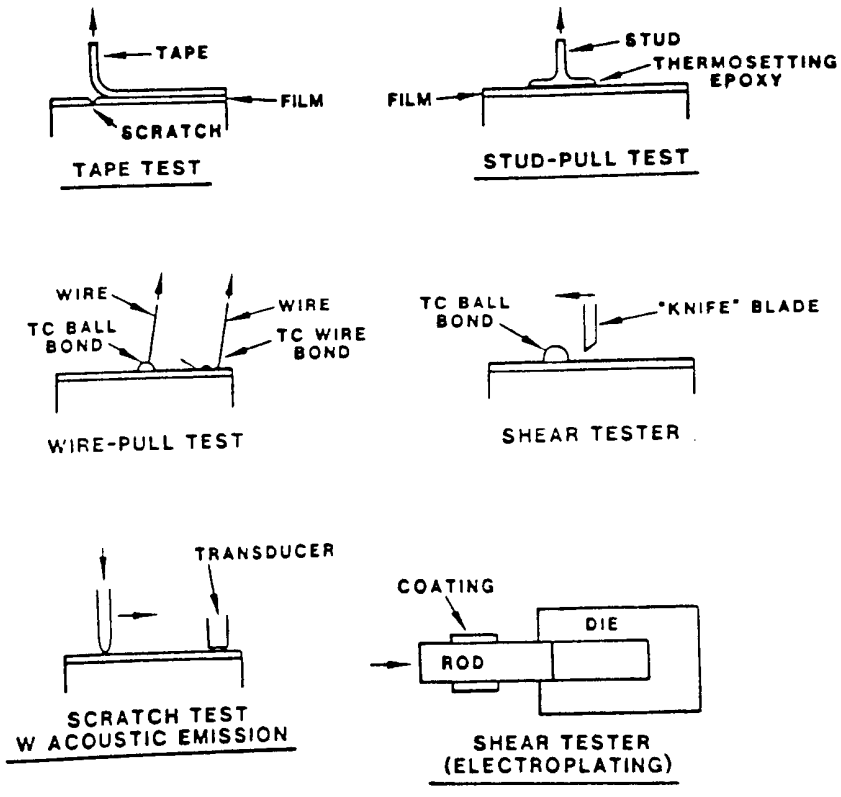


Figure 11-4. Adhesion tests.

Mechanical Pull (Tensile, Peel) Tests

The stud-pull (pull-off) tensile test is performed by bonding a "golf-tee-shaped" stud to the surface of the film using a thermosetting epoxy glue and then pulling the stud to failure.[110] Commercial equipment is available for this test which will measure tensile strengths to 10,000 psi. A major factor in the reproducibility of this test is the amount of adhesive on the surface. Too much adhesive gives "squeeze-out" and a peeling stress around the edges of the stud.

A possible low-contamination pull-to-limit stud pull test might be developed using ice as the bonding agent[111][112] instead of an epoxy

glue. Ice adheres well to surfaces and on melting would leave little contamination. In addition ice expands on freezing so it would put the edges of the bond under compression and not tension (peel) which is the case with shrinkage bonds.

Wires may be joined to surfaces using thermocompression ball bonds or wire bonds, solder bonds, sonic bonding techniques, etc.[113] The wires may then be pulled to evaluate adhesion. These bonding techniques duplicate the bonding techniques used in fabrication. A possible problem with these tests is that the bonding method (heat, pressure, etc.) can degrade the adhesion. For example, bonding tool pressure can fracture the glass surface under the film leading to apparent low adhesion.

The peel test is common for measuring polymer adhesion and a variation of the peel test is the tape test where an adhesive tape is stuck on the film surface then a peel test is performed (*ASTM D3359 "Standard Methods for Measuring Adhesion by Tape Test*).[114] This test is good for detecting poor adhesion (up to about 1000 psi) but is very sensitive to the technique used. The type of tape, method of application, angle of pull, pull rate, etc. are all important test variables. Much of the energy applied in the test goes into deformation of the tape.[115][116] The tape should be pulled over a cut (scratch) through the film since this edge allows the fracture to initiate at the interface otherwise the film can act like a "drum-head" and not fail even though the bond is weak. The tape test has the advantage that small "pullouts" may be detected on transparent tape after it has been pulled from the surface.The tape test is often used in testing optical coatings.

Residual adhesive, which often contains chlorine ions, is a major concern when using the tape test on surfaces that are going to be subsequently processed or used. Most adhesives are very corrosive and unless completely removed, residual contamination can cause corrosion and adhesive failure in the long term. A neutral pH, water soluble adhesive (Filmoplast®) is available on adhesive tapes used for archival photography and is recommended if there is any question of residuals and corrosion. However, this tape does not have the adhesive strength of the more acid-based adhesives.

A version of the peel test is the stressed-overlay-film test. In this test, an adherent film with a known residual film stress, is deposited on the film to be tested. The film stress then causes failure in the film-substrate interface. Using this test, the adhesion of titanium films to silicon has been measured to 30 MPa (4000 psi).[117] The topple test is a type of peel test where the stud is bonded to the film and pushed from the side to give a rotating or peeling motion.[118]

Mechanical Shear Tests

The push-off shear test or die shear test is normally done by "pushing-off" a bump bonded to the film. The force to shear the bump from the surface is measured with a load cell. This test is commonly used in the microelectronics industry.[119]–[121]

The lap shear test utilizes surfaces that are bonded together and then pulled in a shear mode.[122]–[124] This test is commonly used to evaluate adhesive bonds between solid flats but can be used for measuring film adhesion by having one or both of the flats coated with a film. The test is normally performed on a common tensile test machine.

In the ring shear test, a thick coating is deposited on a cylindrical rod. The coating is then machined so as to form a ring with a sharp edge. The rod is then inserted into a close-fitting cylinder and the ring of coating material is sheared from the rod surface. The measured adhesion is sensitive to interfacial roughness since the primary forces are shear. This test is used in the electroplating community.[125]

Scratch, Indentation, Abrasion, and Wear Tests

The scratch (or stylus) test is an old adhesion test method which evolved from the scrape test.[126] In the scratch test, a stylus is drawn over the film surface with increasing load. Under the point-loading, the film and substrate underneath the film is deformed, giving a complex stress to the film/substrate interface. The failure mode of the film is observed under a microscope and a "critical load" at failure is assigned rather subjectively.[127]–[132] The use of an SEM with an *in-situ* scratch testing capability allows the observation of the failure and material transfer without environmental effects.[133] The scratch test can be combined with acoustic emission to give an indication of the onset and magnitude of failure.[27][28][134] The hardness of the substrate material has a significant affect on the scratch resistance (cracking) of thin coatings during testing. Commercial scratch test equipment with acoustic emission detection capability is available.

When the film is relatively thick, the film/substrate can be sectioned and polished so the scratch can be made normal to the interface.[135] This technique avoids some of the uncertainties encountered when the scratch is on the surface of the film.

Surface indentation using a loaded point can be used for adhesion testing in much the same way as the scratch test. Indentations are made with varying load and tip geometries[136] and the area around the indentation is observed for fracture, flaking and deadhesion of the film from the substrate.[129][137] An instrument that can be used for performing this test is the common indentation hardness testers.

Mechanical Deformation

An elongation test can be performed by elongating the substrate and observing fraction and spallation of the film.[138] Bending a substrate around a given radius and looking for spallation (bend test) is used as an adhesion test. The tape test can be applied to the deformed film to show if the failure extended along the interface or just crack the film by extracting any "pullouts."

Stress Wave Tests

In the stress wave adhesion tests, a stress wave is propagated through the system and the reflection of the stress wave at the interface results in a tensile stress at the interface. The stress wave can be injected into the solid from a flyer plate,[139][140] a flyer foil or a laser pulse.[141]–[143] Conceptually the stress wave technique could be used to initiate then stop an interfacial fracture so the fracture initiation could be studied. The onset of the fracture might be detected by acoustic emission. A small-area low-thickness flyer "plate" can be generated by depositing a film on the end of a fiber optic then spalling the film off with a laser pulse.

Fatigue Tests

Thermal stress adhesion testing is used on coatings intended for high temperature applications. The tests often use repeated thermal cycling (thermal fatigue) to test coatings such as such as thermal barrier coatings and coatings for fusion reactor applications.[99][100] A major factor in these tests is the differences in thermal coefficient of expansion of the materials and the deformation properties of the film and substrate materials.

Other Adhesion Tests

Other adhesion testing uses exposure to corrosive or weathering environments. Each industry/application develops tests which they deem suitable for their application. Often these tests include other features such as discoloration or loss of reflectivity as well as evaluating adhesion.

One of the more weird adhesion tests is the "Mattox bad breath test." In this test, a person breaths on the film to condense moisture. If the film has a high residual stress, this stress will try to propagate fractures and the moisture accelerates fracture propagation. When the film fails it will blister or flake. Obviously the uninformed individual, attributes the failure to the "bad breath" of the tester. This test has the advantage that it can be done immediately and without equipment. If the film can not pass this test it will probably fail in the future. The condensing breath contaminates the film surface and the test could probably be improved to be a nondestructive test.

11.5.3 Non-Destructive Testing

Non-destructive adhesion testing techniques would be highly desirable but are of limited availability and reliability. One adhesion test that is commonly used is testing-to-a-limit where a wire bond is pulled to a given force and if it does not fail, the wire bond is used. Tape tests have been used to test a film and then the surface cleaned and used however this can leave potentially corrosive residues. In IC (integrated circuit) manufacturing, conductor stripes can be inspected using infrared (IR) microscopy to find "hot spots" (high resistivity, poor adhesion) or an SEM, in the secondary electron imaging mode, can be used to look for areas of voltage drop (high resistivity, opens) in the conductor lines.

Acoustic microscopy[144] or ultrasonic inspection can be used to visualize large areas of deadhesion ("holidays") in some cases. Mechanical response to vibration has been used to evaluate adhesion as have surface acoustic wave (SAW) devices.[145]

Acoustic Imaging

Some flaws can be imaged using focused acoustic waves using short wavelength ultrasound.[146] Ultrasonic frquencies range from about

5–200 MHz. The ability to transmit a high frequency sonic wave (impedance) depends strongly on the elastic properties of the material and internal features and defects such as interfaces between solids in contact. For example, the relative impedence of some materials are: Air/vacuum = 0, water = 1.5, glass = 15, copper = 42 and tungsten = 104. Analysis can be done by either using the ultrasound in a transmission mode or in a reflection (pulse echo) mode. For the analysis of the interface between the coating and the substrate, the pulse echo mode has the higher resolution and is capable of detecting interfacial delaminations less than 1 micon in extent. The coating has to have an appreciable thickness which depends on the material. Acoustic imaging is the basis for the Scanning Laser Acoustic Microscope (SLAM) where the laser detects surface motion caused by the acoustic wave.

Scanning Thermal Microscopy (SThM)

The Atomic Force Microscope (AFM) can be used to image the thermal pattern over a surface by having a thermocouple junction on the probe tip of an Atomic Fore Microscope (AFM) and the technique is called Scanning Thermal Microscopy (SThM).[147] Thermocouple junctions 100–500 nm in diameter have been produced that have a 10 nm resoultion (low-to-high temperature).[148] By sending a thermal pulse through the substrate differences in surface temperature may indicate poor thermal contact.

11.5.4 Accelerated Testing

Methods of accelerating the degradation modes for accelerated adhesion testing should reflect the same degradation modes as are to be found in service. Acceleration may be accomplished by increased temperature, mechanical fatigue, thermal fatigue,[99][100] concentrated chemical environment,[89][149] or by the introduction of interfacial flaws by some technique. Care must be taken to make sure that the acceleration method does not change the degradation mechanism or change the relative importance of the different degradation mechanisms if more than one mechanism is operational.

11.6 DESIGNING FOR GOOD ADHESION

Good adhesion is a fundamental requirement of almost all film-substrate systems and often depends on how the system is to be used. For example, a system that is adherent under shear stress may not be adherent under tensile stress. Good adhesion is determined by a large number of factors many of which are difficult to control without careful processing and process controls related to the substrate surface (chemistry, morphology, homogeneity), substrate preparation (cleaning, activation, sensitization), materials involved, deposition process, and process parameters. Process development, which leads to good adhesion, is often done in an empirical manner aided by some basic considerations as to what factors are most likely to give good adhesion and what properties are detrimental to good adhesion. The generation of a good interface is also important to other properties such as thermal transport and electrical contact resistance, and what might be a good interface for adhesion may not be a good interface for some other property.

In developing an adherent film-substrate system consideration must be given to:

- Selection of substrate and film materials and the necessary processing and processing parameters to satisfy processing and functionality requirements.
- Substrate surface morphology, mechanical properties and chemistry control.
- Substrate surface preparation which affects the nucleation and interface formation in a desirable manner without introducing flaws into the surface.
- Deposition and nucleation of the adatoms on the surface to give a high nucleation density and "fill-in" surface features to give a high contact area and no interfacial flaws.
- Interface formation and the properties of the "interphase" material to give a high fracture toughness.
- Growth of the deposited material so as to minimize residual stresses and develop a film morphology resistant to diffusion and corrosion.
- Postdeposition processing to increase adhesion and stabilize the system.

- Development of processing specifications to insure reproducible processing.
- Adhesion testing to reflect production, storage and service environments (temperature, chemical, humidity, mechanical fatigue, etc.).

Substrates should have a surface chemistry conducive to a high nucleation density of the depositing atoms. Adhesion can generally be improved by roughening the surface (interface) if the rough morphology can be filled-in. However, depositing on a rough surface does change the morphology of the deposited film material which may influence other film properties such as porosity, surface coverage, electrical conductivity and surface roughness. The substrate surface should not be a weak or weakened material. The surface should be homogeneous in properties. Careful substrate specification and acceptance tests will go a long way to prevent adhesion problems.

In multilayer systems, the films are adherent to each other by having interfacial diffusion or reaction. In order to obtain this adhesion, the surface of one layer should not be contaminated before the deposition of the next. For example, in Ti-Au metallization if the titanium becomes oxidized the gold will not adhere to the oxide surface and the adhesion will be poor.

11.6.1 Film Materials, "Glue Layers," and Layered Structures

For best adhesion, the film material should chemically bond to the substrate surface. If the film material has a high elastic modulus, care should be taken to prevent high total residual stresses in the film. This can be done by controlling the deposition parameters or by limiting the thickness of the deposited film. The latter case is often the easiest to use. When depositing chromium, tungsten or other high modulus film material, the film thickness should be limited to less than 500 angstroms unless there is a good reason to go to thicker films.

Often the best approach to obtaining good adhesion and the desired film properties is to deposit a film material that will bond both to the substrate and to another film(s) which has the desired properties (multilayer film structure). This intermediate material is often called a "glue layer." Examples of this approach are found in many of the metallization systems.[150]–[156] Generally only a very thin layer (50–500 Å) of this material is necessary. For example, in depositing electrical conductors on

oxides, titanium is a good material to adhere to the oxide but it has a fairly high elastic modulus and not very good electrical conductivity. Therefore a metallization of titanium (<500 Å)-copper (as needed)-gold (500Å) provides good adhesion, good electrical conductivity and good corrosion resistance on the surface. The titanium forms a chemical bond with the oxide, the copper alloys with the titanium, and the gold alloys with the copper.

11.6.2 Special Interfacial Regions

Graded and Compliant Interfacial Regions

In some cases, the interfacial material may be designed in such a manner as to form a gradation in properties from one material to the other. This gradation may be in the alloy composition (Sec. 9.3) or reactive deposition conditions such as going from Ti to TiN by controlling nitrogen availability (Sec. 9.3.5). Grading may also be in a physical property such as density or in a mechanical property such as yield strength. Compliant materials are ones that deform easily under stress. Generally they are a soft material but may be a low density material.[21][157][158] Such compliant layers can reduce and distribute the stress that appears at the interface.

Diffusion Barriers

In some cases, diffusion barriers are used at the interface to reduce diffusion.[159][160] For example, W:Ti or electrically conductive nitrides such as TiN, are used as a diffusion barrier in aluminum metallization of silicon to inhibit aluminum diffusion into the silicon during subsequent high temperature processing. Barrier layers, such as tantalum, nickel, and nickel-chromium, are used to prevent diffusion and reaction in metallic systems. The presence of compound-forming species in the depositing material reduces the diffusion rate.[161] Alternatively, materials can be alloyed with film material to reduce diffusion rates.[162]

11.6.3 Substrate Materials

Metals

Good adhesion of metal films to metallic substrates is typically attained by utilizing surface preparation techniques that remove surface contamination and surface barrier layers, then depositing a material that will readily alloy with the substrate material.[150] Elevated surface temperatures aid in interfacial diffusion and often increases the adhesion but "overdiffusion" can decrease adhesion by generating a weak interphase material. Non-soluble metal-metal couples such as Ag-Fe, Au-Ir, Au-Os should be avoided. However, good adhesion can be attained with non-soluble metal systems if the nucleation density can be made high by some techniques such as deposition by ion plating.

Obtaining good adhesion of compound films to metallic substrates is often accomplished by grading the interfacial region.[157] This is often done by controlling the availability of the gaseous reactant. For example, in depositing TiN the first few monolayes would be titanium which would diffuse into the metallic surface and then the nitrogen availablity would increase to finally form the TiN compound material. In some cases, an interfacial layer can be used. Nickel is often a good material since it alloys with most metals and is rather ductile.

All metals, with the exception of gold, form natural oxides. In many cases, the metal oxide is stripped during the external cleaning process and the small amount that is reformed after cleaning is removed by *in situ* cleaning in the deposition system. If the natural oxides on the surface are not removed, then the depositing film material should be an oxygen-active material since the deposition is really onto an oxide surface.

Oxides

Oxide surfaces may be on ceramics, glasses, or metals. Adhesion to oxide surfaces is generally attained by having a contaminant-free surface and using an oxygen-active film material such as Ti, Cr, Mo or Zr.[151][152] To avoid stress problems, the film thickness should be limited (<500Å) and the desired film properties generated using a multilayer film structure.

Examples of adherent metal-to-oxide metallization systems are:

Ti , Ti - Au, Ti - Pd - Au, Ti - Pd - Cu - Au
Cr, Cr - Au, Cr - Pd - Au, Cr - Pd - Cu - Au, Cr - Ag, Cr - Pd - Ag
(Ni,Cr), (Ni,Cr) - Pd - Ag
Mo, Mo-Au
Al

(Note: A-B indicates a layered structure, (A,B) or (A,%B) indicates an alloy, AB indicates a compound.)

If the adatoms are not strongly oxygen-active then a surface chemistry or deposition technique conducive to forming a high nucleation should be used (Sec. 9.2.2). In some cases, the nucleation density can be increased by beginning the deposition with some residual oxygen in the environment or adsorbed on the substrate surface, which is gettered by the initial depositing film material.[83] In some cases, such as the deposition of silver on glass, a high initial deposition rate increases the nucleation density on the surface. The surface chemistry of complex oxide surfaces such as glasses may be altered by selective treatment to change the composition and thus the nucleation of the adatoms on the surface.* For example, a high-lead glass can be dry-hydrogen fired to reduce the surface lead-oxide to free lead which can then act as a nucleating agent for the depositing atoms.

An interesting technique for attaining good adhesion of gold to an oxide surface is by depositing the material in a oxygen plasma.[163]–[168] Unfortunately the adhesion is degraded by exposure to water vapor. In deposition of a compound film on an oxide, good adhesion can be attained by generating a graded type of interface and being sure that minimal stess is generated.

Semiconductors

Adhesion to semiconductor materials generally requires a high nucleation density and the formation of a diffusion or compound type of

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*When float glass is prepared, the side in contact with the tin has a tin oxide coating which is generally removed by etching. If the oxide is not removed, the film nucleation will be different on the two sides of the glass. I mentioned this in one class and a student got up and left saying he had found the answer to his problem. I never saw him again.

interface. Often the system has a requirement for a low electrical contact resistance and good resistance to electromigration in addition to good adhesion.[169][170] This can often be accomplished using a layered structure.

Examples of adherent metal-semiconductor systems include:

[Note: A-B indicates a layered structure, (A,B) or (A,%B) indicates an alloy, AB indicates a compound.]

On silicon[92][171]
Al, (Al,1-3%Cu), (Al,1%Si), (Al,1%Si,2-4%Cu)
W
WSi_2 - W
Mg - Al
Cr - Mo
(Ti, 10%W)
TiN - W
TiN - Al, TiN - (Al,1%Si,2-4%Cu)
PtSi, PtSi-Pt

On GaAs[172]
(Au,Zn,Ni) - Ti - Au
(Au,Ge) - Ni

In some cases barrier layers are used to prevent interdiffusion during subsequent high-temperature processing.

Polymers

In order to attain good adhesion, the polymer surface should be free of contaminants and low molecular weight fractions (weak surface layer). Adhesion to polymers can be attained by using a film material that will form organo-metallic bonds with the substrate such as Al, Cr or Ti.[173]–[175] The polymer surface can be plasma treated to make them more chemically reactive which increases the bonding and nucleation density (Sec. 2.6.5).[176]–[182] Generally oxygen or nitrogen plasmas are used for activating the surfaces. The oxygen plasmas treatment make the surfaces more acidic owing to the formation of carbonyl groups (C=O) on the surface. Nitrogen or ammonia plasma treatments make the surfaces more basic, owing to the formation of amine and imine groups “grafted” to the surface. Surfaces can be over-treated with plasmas, creating a weakened

near-surface region and thus reduced film adhesion. Some increase in adhesion can be attained by roughening the surface and having mechanical interlocking between the deposited film and the surface. Nucleating species may be incorporated into the surface by chemical treatments.

Examples of adherent metal-polymer systems are:
[Note: A-B indicates a layered structure, (A,B) or (A,%B) indicates an alloy, AB indicates a compound]:

Polymers
Al
Cr - Au
Nichrome IV (80%Ni,20%Cr) - Au
Inconel (76%Ni,8%Fe,16%Cr) - Au

11.7 FAILURE ANALYSIS

Failure analysis is very specific to the individual problem but some general questions should be asked.

- Is the failure in the interface or in the substrate or film material?
- Is the failure due to subsequent processing or application rather than due to the PVD processing?
- Was the process under control when the films were deposited (i.e., was there a flow chart and appropriate documentation)?
- Were there any significant changes in the processing at the time of fabrication (from MPIs and Travelers)?
- Were there any changes in equipment performance when the films were processed (from MPIs and Travelers)?

11.8 SUMMARY

Adhesion is a fundamental requirement of almost all film systems and is determined by the nature of the stresses that appear at the interface and the energy needed to propagate a fracture and/or cause deformation. Film adhesion is intimately connected with the nucleation,

interface formation, and film growth as well as the properties of the interfacial (interphase) materials. Good adhesion is promoted by: high fracture toughness of the interface and the materials, low concentration of flaws, presence of fracture blunting and deflecting features, low stresses and stress gradients, absence of fracture initiating features, and no operational adhesion degradation mechanisms. Poor adhesion can be attributable to: low degree of chemical bonding (as evidenced by a low nucleation density), poor interfacial contact, low fracture toughness (brittle materials, flaws), high residual film stresses, fracture initiating features and/or operational adhesion degradation mechanisms.

Poor adhesion may be localized so as to give local failure on stressing. In many systems where direct adhesion is difficult to attain, a material ("glue layer") can be introduced onto the substrate surface to bond to the substrate and the film material. Substrate surface roughness can improve or degrade the adhesion depending of the ability of the deposition technique to fill-in the surface roughness (surface covering ability) and the film morphology that is generated. The generation of a good interface is also important to other properties such as thermal transport and electrical contact resistance. The loss of adhesion is often called deadhesion in the literature.

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12

Cleaning

12.1 INTRODUCTION

The condition and reproducibility of the substrate surface is an integral part of any PVD processing. In most cases, the surface condition will be determined by cleaning to remove undesirable contaminants from the surface. In some cases, the surface will be used without any cleaning. However, the as-received condition of the surface should be known and specified. For example in web coating, the substrate is in the form of a polymer film that is several tens of thousand feet long. The web is used as-received from the manufacturer being unwound and rewound in the deposition chamber.

A contaminant can be defined as any material on the surface that interferes with the film formation process, affects the film properties in an undesirable way, or influences the film stability in an undesirable way. In most cases, the concern is with both the type and amount of the contaminant. Contaminants can cover the whole surface such as oxide reaction layers or adsorbed hydrocarbon layers, or they can be limited to restricted areas such as particles or fingerprints. A major concern in processing is the variability of the contamination in such a manner as to affect product reproducibility.

Recontamination is contamination picked up after the cleaning process and before the deposition process. This recontamination can occur in the external processing environment or in the deposition chamber before the deposition begins. Figure 12-1 shows the recontamination of a

clean gold surface when exposed to the ambient as measured by the coefficient of adhesion.[1] Recontamination was by adsorbed vapors from the atmosphere.

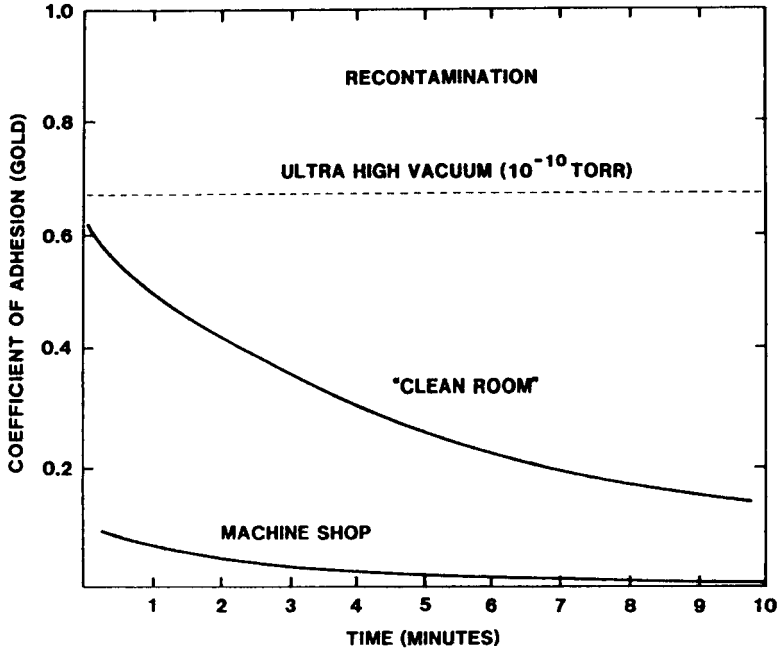


Figure 12-1. Recontamination of clean gold surfaces in different environments as a function of time.[1]

Cleaning is the removal of surface contaminants and is part of what can be termed surface preparation which can also include surface treatments (surface modification) to change the properties of the surface in a desirable way (Sec. 2.6). Care must be taken to ensure that the surface preparation processes do not change the surface in an undesirable or uncontrolled manner. One objective of any surface preparation procedure is to produce a homogeneous surface. Reproducible surface preparation, as well as associated handling and storage techniques, are obtained by having appropriate written specifications and procedures.

Cleaning is the reduction of surface contamination to an acceptable level so that desirable processing and film/coating properties can be obtained.[2] As a practical matter a clean surface is one that contains no significant amounts of undesirable material; thus what constitutes a clean

surface depends on the requirements. The requirements range from those concerned with monolayer coverages and atomically clean surfaces,[3]–[5] to gross cleaning such as used for fusion welding. General contamination such as a surface layer can cause a low nucleation density of the depositing film on a surface, cause poor overall adhesion of a film to a surface, and prevent good electrical contact in the case of deposited electrical contacts. Local contamination (film or particle) can result in locally poor adhesion of a film to a surface giving pinholes in the film. Figure 9-1 shows how pinholes are formed in deposited thin films by particulate contamination on the surface, inclusions in the surface, or by surface features. Cleaning should address local surface conditions such as porosity, embedded particles, steps, roughness, etc. that affect film properties, produce pinholes, and local loss of adhesion.

There are many choices for cleaning.[6][7] The objective of cleaning processes is to facilitate the fabrication of an acceptable product in the most reproducible and economical way. Cleaning processes should be as simple and effective as possible in order to meet the processing requirements. Elaborate cleaning processes are often expensive and self-defeating. Often there is a tradeoff between the various stages of the cleaning process, handling/storage and previous, as well as, subsequent processing.[8] This can mean that simple changes in one stage make complex changes in another step unnecessary. For example, raising the deposition temperature usually allows for lower cleaning requirements in order to get good adhesion. The processing sequence as a whole should be considered when developing a cleaning process.

Cleaning can be divided into external cleaning (*ex situ* cleaning) that is performed exterior to the deposition system and where the external processing environment (Ch. 13) is important, and in situ cleaning that is performed in the deposition system, where system-related and process-related contamination are important. Generally the external cleaning is performed to as great an extent as possible and the *in situ* cleaning is used to remove materials that have recontaminated the surface or that are naturally on the surface such as oxide layers. Important aspects of external cleaning are having a controlled processing environment and handling and storage of the cleaned surface in such a manner as to minimize recontamination. It is often instructive to develop a flow chart for the processing of the substrate material before it is placed in the PVD deposition system (Sec. 1.3). Figure1-3 shows an example of such a flow chart. Specifications and Manufacturing Process Instructions should cover all steps of the processing including handling, storage and transport.

External cleaning includes gross cleaning to remove large amounts of contaminants often by removing some of the substrate surface (etching). Specific cleaning is directed toward removing a specific contaminant such as particulates, or hydrocarbons. If possible, the substrates should be contained in holding fixtures that remove the necessity and potential variability of manual handling of the critical surfaces.

12.2 GROSS CLEANING

12.2.1 Stripping

Stripping is the removal of thick deposits on a surface. For example, stripping is used to remove thick oxide layers by "pickling" and to rework coated substrates as well as cleaning of fixtures and removable vacuum surfaces. Table 3-11 lists a number of stripping chemicals for removing deposits from substrates, fixtures and other surfaces.

12.2.2 Abrasive Cleaning

The removal of gross contamination by abrasive cleaning includes the use of:

- Abrasive surfaces—e.g., sandpaper, emery paper, steel wool, Scotch-brite™ and Soft-scour™ scouring pads, etc.
- Abrasive powders in a paste or fluid carrier—e.g. SiC, Al_2O_3, diamond, precipitated calcium carbonate ($CaCO_3$), CeO, talc, kaolin, wheat starch, and Snow-Floss™ (diatomaceous earth with the calcium carbonate removed leaving a friable silica network).*
- Impacting particles entrained in a high velocity gas or liquid stream—e.g. vapor honing, glass bead blasting, liquid honing, grit blasting, sand blasting, etc.[9]

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*A good cleaning procedure had been developed for depositing an adherent molybdenum film on an alumina substrate. It was decided that the alumina surface should be roughened using 5 micron metallurgical polishing paste. After the roughening treatment, the surface just could not be cleaned. Investigation showed that the polishing compound had a silicone-like binder that was resistant to all cleaning procedures. A switch was made to a polishing paste that had a water soluble binder and the cleaning problem was resolved.

- Abrasives combined with an etchant to provide chemical-mechanical abrasion and polishing.

Abrasive particles can be used wet or dry with various particle sizes (grits). Commercially available abrasive particles include aluminum oxide, silicon carbide, diamond, glass beads, fractured cast iron, silica sand, cerium oxide, plastic blast media, and sodium/potassium carbonates (water soluble).[10] The average size of particles produced by screening can vary between the different types of grit. Table 12-1 shows the particle size for some materials. Abrasion cleaning can be very mild such as the use of CeO polishing slurry in a high throughput wash system to preclean glass before the standard wash cycle.[11] When such a slurry is used the viscosity should be monitored.

Dry glass bead blasting is a commonly used cleaning technique[12][13] but, as with most other grit abrasive techniques, can leave chards of glass embedded in soft surfaces. The amount of grit embedded depends on how long the glass beads have been used (i.e., how much they have been fractured).[14] Water soluble particles can be used for abrasive cleaning and allow easy removal of the water-soluble embedded particles.[10] For example, the Prophy-jet™ dental abrasive unit uses 5 micron sodium bicarbonate (baking soda) particles entrained in a high velocity water stream.[15] Typically the baking soda abrasive particles are larger than those used in the kitchen. Baking soda stripping and cleaning was used to clean the Statue of Liberty (copper).

Grit blasting uses grit such as fractured cast iron, alumina, silica, etc., of varying sizes and shapes accelerated in a gas stream to deform and gouge the surface. Particles can be entrained in a high velocity gas steam by using a siphon system or a pressure system such as used in sand blasting equipment. In addition to removing gross contamination, grit blasting roughens the surface, introduces microcracks into the surface of brittle materials, and introduces compressive stresses into metallic surfaces. The Society of Automotive Engineers (SAE) has specifications on grit size and type, e.g., *SAE Specification J444* for cast iron grit in the range G10 (2820 microns maximum size) to G325 (120 microns maximum size) which specifies the percentage by weight allowed on standard screens (Table 2-3). Bombardment of a surface by grit is like “shot peening” and places the surface in compressive stress which may produce unacceptable distortion of the surface. Blasting can also be done with plastic media which is less damaging than the harder grits; however it can leave organic contamination on the surface.[16]

Table 12-1. Average Particle Size (microns) of Some Abrasive/Polishing Materials

		Grit/Mesh Size	Emery	Al_2O_3 SiC/Garnet	B_4C	Diamond
		24		1035	710	1036
	A	30		930	590	
C	B	36		810	500	712
O	R	46		508	350	508
U	A	54		430	297	
R	S	60		406	250	407
S	I	70		328	210	
E	V	80		266	177	267
	E	90		216	149	
		100		173	125	213
		120		142	105	142
		150		122	74	122
	A	180		70–86	62	86
F	B	220		66	53	66
I	R	240		54–63	42.5	60
N	A	280	1	44	35	
E	S	320	1/0	29–32	27.7	52
	I	400	2/0	20–23	16.3	40
	V	600	3/0	12.5–17	8.3	14
	E					
P		800	4/0	9–12	5.5	8
O		1000		5–9	3.7	
L		1200		1.5–5	2.5	6
I		1500		1–1.5		4
S		2000		1.0		2
H						1
						0.5
						0.25

Wet blasting uses a high-pressure water stream (to 50,000 psi) or an air-blasted slurry of fine abrasives in chemically-treated water. The liquid slurry is sometimes called liquid honing since it is usually used when dimensional tolerances have to be maintained.

12.2.3 Chemical Etching

Chemical etching can be used to remove surface material along with the contaminants.[17][18] This is a very useful technique for achieving a "known" surface condition. Chemical etchants can be highly selective in their action. This can result in preferential etching of grains when etching a two phase system. Pickling is a term used to denote the removal of the large amounts of oxides ("scale") that is formed on metals during the metal fabrication process. Generally removing scale involves an alkaline clean, prior to acid pickling, in order to get uniform wetting and etching.[19] For example, aluminum and aluminum alloys can be pickled by immersion in various combinations of sulfuric, nitric, hydrofluoric and chromic acids; copper and copper alloys can be pickled in combinations of sulfuric and oxidizing acids; and iron and steel can be pickled in sulfuric or hydrochloric acid solutions. Mild pickling is called a bright dip. Acid cleaning of metals can have the detrimental effect of introducing hydrogen into the surface and embrittling metals and ceramics.[20] If hydrogen embrittlement is a concern, either do not use an acid or the etched part should be high-temperature vacuum baked after etching.

Chemical etching can be used to remove surface layers such as oxides, eliminate or blunt surface cracks in brittle materials, and remove strongly adherent contaminates. Common etchants for glass include sodium or ammonium bifluoride (100 grams of ammonium bifluoride salt in 800 cc deionized water), trisodium phosphate (a mild etchant), and hydrofluoric (HF) acid (a very strong etchant). For example, a mild HF etch (1:100) is used in cleaning glass for flat panel display production.[21] Hydrofluoric acid solution is a common etchant for silicon[22][23] and can leave a silicon surface either hydrogen-terminated or hydroxyl-terminated.[24] The silicon surface is hydrophobic ("water-hating") if hydrogen-terminated, and hydrophilic ("water-loving") if hydroxyl-terminated.

When using etchants for cleaning, care must be taken to prevent selective removal of surface constituents that are important to further processing. For example, etching glass-bonded alumina ceramics (Fig. 2-2) in HF results in selective removal of the glass [Ca-Mg-Al-Si-O] phase which can weaken the ceramic surface and result in poor adhesion.[25] Etchants can change the surface chemistry. For example, acid etching a soda lime glass surface, which is normally basic, leaches the sodium from the surface and makes the surface acidic.[26]

Sometimes chemical etching does not remove some constituents from a surface and leaves a smut that must be removed by further etching. For example, etching aluminum-copper-silicon alloys with sodium hydroxide (NaOH) leaves a copper smut and/or a silicon smut on the surface. The copper smut can be removed by a nitric acid (HNO_3) etch and a copper/silicon smut can be removed with a HNO_3/HF etch. In some cases, an etchant can be devised that etches all the constituents uniformly. For example, in etching Al:Cu:Si alloys, a concentrated nitric acid (100 cc) plus ammonium bifluoride (6.8 g) etch is used. The etching mechanism is solution of the copper, oxidation of the aluminum and the silicon, then etching of the resulting oxides. The etchant actually etches silicon more rapidly than the aluminum.

A version of chemical etching of silicon uses HF vapor instead of a liquid phase.[27][28] Vapor phase etching has an advantage over wet chemical etching of complex surface geometries in that wetting of the surface is not the problem that it is in wet etching. In this technique, the wafer is contained in a chamber of silicon carbide, the chamber evacuated and backfilled with an azeotropic mixture of HF/H_2O (38.4 wt percent HF). After etching at 30–50°C the surface is "rinsed" using water vapor at 60°C. Another example is the etching of SiO_2 in wet HF gas to produce better cleaning than in an HF solution.[29][30] Laser heating has been used to enhance vapor phase etching.

12.2.4 Electrocleaning

In an electrolysis cell the surface of an electrical conductor can be removed by making it the anode of an electrolytic cell and "off-plating" the material (i.e., the inverse of electroplating). This is called electroetching or electrocleaning and generally produces a roughened surface, with the higher the current density the more roughened is the surface. For example, tool steel and tungsten can be anodically electroetched in 10–20% sodium hydroxide at 200 A/ft^2 at 160°F and stainless steel is anodically cleaned in a sulfuric acid electrolyte. At the anode of an electrolysis cell, oxygen is released which can react with the surface to oxidize contaminants on the surface at low anodic potentials. For example, the surface of stainless steel is oxidized (passivated) at low potentials and etched at higher potentials.[31] Carbon can be anodically cleaned and deburred by oxygen in the electrolysis cell (Sec. 12.3.4).

Electroless electrolytic cleaning relies on the difference in electromotive potentials to remove material from one surface and deposit it on another (i.e., displacement plating, Sec. 1.1.2). For example, a displacement-type electrolytic cleaning process for very delicate silver surfaces is to immerse the silver surface in an undiluted solution of pure household ammonia contained in an aluminum[32] or magnesium tray. The silver surface is cleaned as the aluminum or magnesium is oxidized. Most commercial silver cleaners are thiorea-based, which leaves a corrosion-product layer on the surface.

Electropolishing anodically removes material and smoothes the surface.[33] The smoothing action is due to protection of the smooth areas by a deposited phosphate material, and the erosion of the exposed peaks. Electropolishing leaves a phosphate film on the surface which can be removed by leaving the surface in the polishing solution without any applied voltage or with an HCl rinse.

12.2.5 Fluxing

Fluxes remove oxides by dissolving or undercutting them and floating the surface layers away.[34][35] Fluxes are commonly used in welding and soldering but not commonly used in cleaning for film deposition. However, gallium and indium have been used to "flux clean" silicon surfaces in vacuum.[36,37]

12.2.6 Deburring

Deburring is the removal of the rough edges (burrs) that are produced in cutting or shearing. Deburring is performed by abrasion, chemical etching or by "flash deburring" when a "flame front" from an explosion, heats and vaporized the burrs.

12.3 SPECIFIC CLEANING

There are a number of cleaning agents and techniques that can be used for specific cleaning.[38] The number is growing all the time. A major

factor in assessing new cleaners is their compatibility with the surface to be cleaned, their safety and their environmental acceptability.

12.3.1 Solvent Cleaning

Some contaminants can be removed from surfaces by solvents which dissolve (take into solution) the contaminant. Polar solvents such as water and water-alcohol mixtures are used to dissolve ionic materials (salts) which are polar contaminates. Non-polar solvents such as the chlorinated hydrocarbon solvents, are used to remove non-polar contaminates such as oil. Often there is a mixture of solvents to dissolve both polar and non-polar contaminates. Solvents can vary greatly as to their ability to dissolve contaminants and their effectiveness needs to be determined by determining the solubility parameter (e.g., Kauri-Butanol Value) for specific contaminants. The solubility parameter is the maximum (saturation) amount of a specific contaminant that can be dissolved in a specific amount of the solvent. Solvents can be used at room temperature (cold cleaning) or at an elevated temperature.[39] Generally increasing the temperature increases the solubility parameter.

Solvent cleaning can leave a surface layer of residue which must be removed. This removal can involve either water rinsing, other solvents that displace the surface layer, or an elevated temperature. For instance, a solvent wipe-clean cleaning sequence might be: trichloroethylene—acetone—methanol—isopropanol.

Volatile organic compounds (VOCs) are those that have boiling points below 138 ^{0}C. The discharge of many VOCs into the environment is regulated by local, state and federal laws. In order to comply with these regulations it may be necessary to recycle the material by condensation of the vapors or to thermally destroy the vapors by burning[40] before they are released into the atmosphere.

Water

Water and water-alcohol mixtures (typically in a ratio of 1:1) are good polar solvents for a variety of polar contaminants such as ionic salts. The addition of alcohol lowers the surface energy of the water and allows it to penetrate into “hideouts” to remove hidden contamination (Sec.

12.3.3). Water and water-alcohol mixtures are not good solvents for non-polar contaminants such as oils.

Petroleum Distillate Solvents

Solvents such as mineral spirits, kerosene, white spirits, naptha, Stoddarts Solvent, PD-680 (US Military), gasoline, and diesel fuel oil, consist of materials that have a broad range of boiling points and generally have low flashpoints that limits their application. Paraffinic hydrocarbons can be produced that have a high degree of purity and a flashpoint above 140°F. These cleaners are generally used when contact between the surface to be cleaned with water is not desirable. Though petroleum-based solvents are often effective in removing large amount of contamination, surfaces cleaned in petroleum solvents can be expected to have residual contamination that may have to be removed.

Chlorinated and Chlorofluorocarbon (CFC) Solvents

Chlorinated hydrocarbon solvents such as trichloroethylene (TCE) are often preferred to hydrocarbon-based or petroleum-based solvents because of their lower flammability (i.e., higher flashpoint as determined by *ASTM D1310-63*). However there is concern with the toxicity and carcinogenic properties of some of these materials and they should be used in well ventilated areas. Solvents containing chlorine and fluorine (chlorofluorocarbons, CFCs) do not have carcinogenic problems and often have been used where large quantities of solvents are required. The ability of CFCs to dissolve contaminants is generally less than that of the chlorinated solvents so larger volumes of solvents are used.

The well substantiated atmospheric ozone depletion[41] and the controversial increase in the "greenhouse effect" have put the use of many common chlorinated and chlorofluorocarbon materials (CFCs) in question. These solvents vary greatly in their potential for ozone depletion and atmospheric warming and a rating system has been devised based on their ozone-depletion potential (ODP) and their Global Warming Potential (GWP). On Dec 31, 1995 all US producers ceased production of fully halogenated CFCs although recycled solvents will be available for some time and the solvent will still be manufactured by off-shore manufacturers

and can be imported under license. The use of CFCs (and HCFCs) will be phased out except for applications where they can be completely contained.

A common chlorinated solvent is 1,1,1-trichloroethane (TCA - $CHCCl_3$) (or methyl chloroform) which has been widely used in vapor degreasers. TCA has a high Permissive Exposure Level (PEL), is classed as non-volatile and has low toxicity however it has a high ODP rating. To meet EPA standards, the vapors must be contained. This means that the old-style vapor degreasers, which are open to the atmosphere will have to be replaced with enclosed vapor systems as shown in Fig. 12-2.

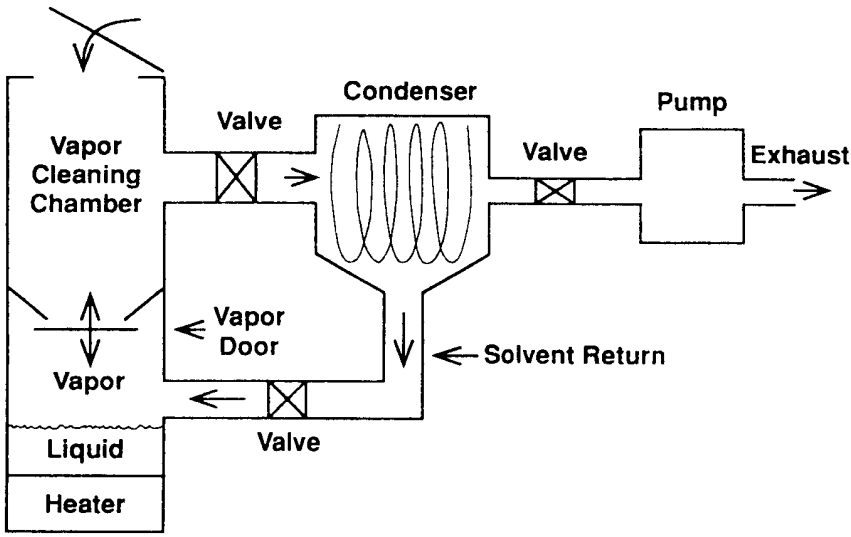


Figure 12-2. Enclosed vapor cleaner and dryer.

A possible alternative to TCA for many applications is methylene chloride (MEC - CH_2Cl_2). MEC has a rather low PEL so the vapors must be contained. This is rather difficult since MEC has a boiling point of 39.8°C. This low boiling point makes it applicable as a solvent for vapor degreasing temperature-sensitive materials. MEC is a very aggressive solvent and can damage plastics and rubbers.

Perchloroethylene (PCE or PERC - $Cl_2C{:}CCl_2$) has a high boiling point (121.1°C) and is useful for dissolving heavy greases. PCE has a

rather low PEL and so the vapors must be contained. PERC can contain a large amount of water without degrading its solvency powers.

Trichloroethylene (TCE - $CHCl:CCl_2$) has excellent solvency and a medium boiling point of 87°C. Emission standards make containing the TCE vapors a requirement. TCE is an excellent candidate for replacing TCA in enclosed vapor degreasers.

Trichlorotrifluoroethane (Du Pont Freon™ TF or CFC-113 - CCl_2FCClF_2) is a fairly good solvent. Emission standards make containing the CFC-113 vapors a requirement. Table 12-2 provides some properties of common chlorinated and chlorofluorocarbon solvents.

Table 12-2. Common Chlorinated and CFC Solvents

Property	CFC-113	TCA	TCE	PERC	MEC
ODP (Ozone Depleting Potential)	0.8	0.1	-	-	-
RCRA (PhotoChemical Reactivity)	No	no	yes	yes	-
Molecular weight	187.4	133.5	131.4	165.9	84.9
Boiling Point (°C)	47.6	72-88	86-88	120-122	40
Density (g/cm3)	1.56	1.34	1.46	1.62	1.33
Surface tension (dyne/cm)	17.3	25.4	29.3	31.3	-
Kauri-Butanol Value	31	124	130	91	132
Vapor pressure (RT, mm Hg)	285	100	58	14	350
OSHA PEL 8-hr TWA (ppm) (proposed)	1000	350	50	25	<25
Flash point (°C)	>100°C	>100°C	>100°C	>100°C	>100°C

Kauri-Butanol Value—expresses as solvency for Kauri rosin, higher values → higher solubility.

Solvents can be mixed to give synergistic cleaning actions. Typical mixed CFC solvent systems are: (Data from Du Pont solvent formulation data bulletin No. FST-5. Other solvents and solvent blends are available from Du Pont and other manufacturers.)

- Azeotrope mixture of Freon™ TF with methylene chloride (50%) → Freon™ TMC for metal vapor degreasing
- Freon™ TF with ethanol (4%) and nitromethane (1%) → Freon™ TES for removing rosen fluxes and ionic contaminates from solvent sensitive assemblies
- Freon™ TF with ethanol (4%) → Freon™ TE for defluxing
- Freon™ TF with acetone (11%) → Freon™ TA for a broad range of solvency
- Blends of Freon™ TF with methanol (6%) and nitromethane (0.25%) → Freon™ TMS for defluxing
- Freon™ TF with anhydrous isopropanol (35%) + stabilizer → Freon™ T-P 35 for cold cleaning
- Freon™ TF with ethanol (35%) → Freon™ T-E 35 for removal of organics and polar materials

Some solvents can react with the surface being cleaned. For example, chlorinated solvents can react with water to form HCl (sour bath) which can react with many metals, particularly Al, Mg, Be, Zn (white metals), to form inorganic salts. Often stabilizers are added to the chlorinated solvents to reduce their tendency to react with water and form acids. If stabilizers are not used, the pH of the cleaner should be monitored to keep the pH in the 6 to 7 range.[42] If there is a possibility of solvent trapping due to incomplete rinsing, particularly in stressed metal joints, chlorinated solvents should not be used since chloride residues can enhance stress corrosion if moisture is available. Some solvents can cause swelling or crazing of polymer surfaces.[43]

Alternative to CFC Solvents

Even though the CFC materials will be around for a number of years as recycled materials there are a number of non-CFC-containing solvent systems that are being used or are under consideration as alternatives to CFC cleaners.[44]–[47] One desirable factor in the use of CFC solvents is their non-corrosive nature. Many of the proposed replacements for the CFCs are much more aggressive. An interim replacement for the CFCs could be the hydrochlorofluorocarbons (HCFC) which have a lower ozone depletion factor, but these will also be phased out in the near future. Information on CFC replacements can be obtained from Industry Cooperative

for Ozone Layer Protection (ICOLP - phone 202/737-1419) or the EPA's Stratospheric Ozone Information Hotline (phone 800/296-1996).

An example of an material that may be important as a substitute for a CFC is liquid CO_2 (LCO2). LCO2 at 20°C, which is below the supercritical point, has been shown to be a good solvent for cleaning metals.[48] LCO2 has a low surface tension (5.0 dyne/cm) and has a low viscosity (0.07 centipoise). Liquid LCO2 may become a substitute for perchloroethylene (PERC) in the dry cleaning (clothes) industry.

Supercritical Fluids

If a gas, such as CO_2, is compressed to its "critical pressure" (CO_2 = 1077 psi) it liquefies to become a "critical fluid." If it is also heated above its "critical temperature" (CO_2 = 31.1°C) it becomes a supercritical fluid (SCF) as shown in Fig. 12-3. Critical fluids and supercritical fluids are good solvents for many medium-molecular-weight, non-polar or slightly polar organics. The more dense the SCFs are, the better their solvency power.

Solvents can be densified most easily when they are in the supercritical state. Carbon dioxide has been shown to have a Hildebrand solubility parameter[49] which can vary from 0 in the gas phase to 10 under high pressure supercritical conditions (SCF-CO_2 - critical point 31°C, 74 bar pressure). The Values of 6–8 are typical, which is about the same as hexane and carbon tetrachloride and is higher than Liquid-CO_2 (LCO2) for many contaminants. Supercritical CO_2 fluid has the advantage that it is stable, has low toxicity, minimal cost, and is a solvent for many organic materials and has shown promise as a solvent cleaning technique.[50]–[52] Table 12-3 shows typical operating parameters for SCF cleaning.

Table 12-3. Operating Conditions for CO_2-SCF Cleaning

Parameter	Range
Pressure	1450–4350 psi
Temperature	100–185°F
SC CO_2 density	30 – 50 lb/ft^3
SC CO_2 flow rate	2–11 lb/hr
Cleaning time	0.5–3 hours

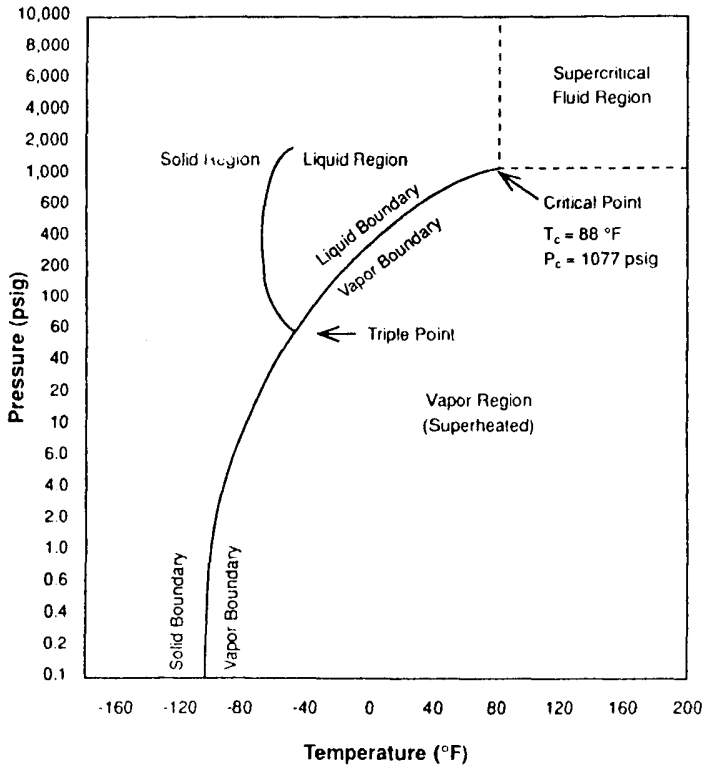


Figure 12-3. Phase diagram for pure CO_2.

Semi-Aqueous Cleaners

Semi-aqueous cleaners refer to cleaners comprised of solutions of natural or synthetic organic solvents which are used in conjunction with water in some part of the cleaning cycle.[53] These cleaners are generally biodegradable. In the metal cleaning industry the semi-aqueous cleaners are also called emulsion cleaners.[54]

Water immiscible semi-aqueous cleaners include terpenes, high-molecular-weight esters, petroleum hydrocarbons, and glycol esters. Terpenes are natural hydrocarbons such as the *d*-limonene and the α- and ß-pinenes, which are derived from citrus and pine oils.[55] Reports indicate that the terpenes may be as effective as the CFCs in many instances though they have a greater tendency to leave residues. Terpenes suffer from the fact

that they are slow drying and have low flash points (about 120 °F) and reduced Lower Explosive Limits (LEL) than the CFCs. Other approaches to CFC replacement use non-linear alcohols and purely aqueous cleaning.[55] Many non-chlorinated hydrocarbon-based or petroleum-based materials are used as solvents. High-molecular-weight esters used in cleaners include alkyl acetates and dibasic acid esters. Many of the alternative solvents are not compatible with plastics. An exception are the perfluorocarbons, which, unfortunately, are poor solvents. The perfluorocarbons can be blended to give better cleaning power. These blends will probably be used as a replacement for CFC-113 for applications involving plastics.[56] This area of solvent development is rapidly changing.

Water miscible semi-aqueous cleaners include low-molecular-weight alcohols, ketones, esters and organic amines. Table 12-4 gives some properties of water miscible cleaners. N-methyl-2-pyrrolidone-based solvents have a high solvency for a number of contaminants and are completely water soluble. Acetone (CH_3COCH_3) removes heavy oils quite effectively but tends to leave a residue and it is also quite flammable. Acetone cleaning or "wipe-clean" should be followed by a methanol rinse or wipe-clean to remove the residue.

Table 12-4. Properties of Some Water Miscible Cleaners (Boiling Point—BP, Melting Point—MP)

Compound	Molecular wt.	BP (°C)	MP (°C)	Density (g/cm^3)
Alcohols				
ethanol (ethyl)	46.07	78.5	-117	0.789
n-propanol	60.11	97.4	-127	0.803
isopropanol	60.11	82.4	-90	0. 786
furfuryl	98.10	171	-14	1.130
Ketones				
acetone	58.08	56.2	-95	0.790
Esters				
(L)ethyl lactate	118.13	154	N/A	1.031

12.3.2 Saponifiers, Soaps, and Detergents

Alkaline cleaners (generally silicate and phosphate-based) are saponifiers which convert organic fats to water soluble soaps.[56] Mild alkaline cleaners have a pH of 8–10 while strong alkaline cleaners (caustic cleaners) have a pH of 12 and higher. Mild alkaline cleaners often have dissolved silicates, carbonates, borates, and citrates and should be used to clean alkaline-sensitive materials such as aluminum and magnesium. A typical strong alkaline cleaner may have water, sodium silicate, sodium molybdate and sodium fluoroborate and have a pH of 12.90–12.99 with a specific gravity of 1.090–1.1055.[57] The sodium silicate may have charged cyclic silicate molecules that develop electrostatic forces that displace the contaminants while depositing a glassy film that prevents recontamination. The glassy material is removed in the DI water rinse. Alkaline cleaners are generally used hot. For example, carbonized hydrocarbon contaminants on glass can be removed by cleaning in a saturated water solution of KOH at 75°C.

After using alkaline cleaners, the surface should be followed by an acid dip prior to the water rinse to remove alkali salts since alkali salts adhere strongly to surfaces and are difficult to remove by water rinsing. Clean oxide surfaces strongly adsorb hydrocarbons, and detergents or solvents normally do not completely remove the hydrocarbons; alkaline or oxidative cleaners must be used to remove the remaining hydrocarbons. Strong alkaline cleaners can etch aluminum and oxide surfaces, particularly glasses, so solution strength (pH), temperature, and exposure time should be carefully controlled.

Detergent cleaning is a comparatively mild cleaning technique.[58] In detergent cleaning, the detergent surrounds contaminants, taking them into suspension (emulsifying) without actually dissolving the material. This emulsifying action is assisted by wetting agents and surfactants which loosen the contaminants from the surface. The most common detergents are soaps which are the water-soluble reaction product of a fatty acid ester and an alkali (usually sodium hydroxide). Liquid dishwasher soaps (e.g., Dawn™ or Joy™) are excellent detergents for many applications such as cleaning polymer surfaces. Soaps clean greases from surfaces more effectively in hard water than in soft water. A major problem with soaps is that metal ions, such as the calcium and magnesium, which are found in hard water, react with ions in the soap, producing an insoluble inorganic residue. De-ionized (DI) water should always be used as a rinse for residue-free detergent cleaning. Many soaps (and other CFC replacement

cleaning techniques) contain chlorine and if a soap residue is trapped on a metal part (e.g., aluminum or stainless steel) it may cause corrosion. Many detergents contain petroleum distillates and phosphates which can be environmentally harmful and subject to pollution regulations when used in large quantities.

12.3.3 Solution Additives

When cleaning a surface with a fluid, the surface energy[59] of both the solid and the liquid, as well as the interfacial energy between the two, are important in the wetting and spreading of the fluid on the surface. Wetting affects the ability of the fluid to displace particles and other contaminants from the surface. Wetting agents reduce the surface energy of fluids. Table 12-5 shows the effect of some additives on the surface tension of water.

Table 12-5. Surface Tension of Fluids

Material		Surface tension (in air)	
Pure H_2O	at 18°C	= 73.05	mJ/m^2 (dyne/cm)
	at 50°C	= 67.91	
	at 100°C	= 58.9	
n-propanol	at 25°C	= 23.32	
Acetone	at 20°C	= 23.7	
H_2O + 30 vol% *n*-propanol	at 18°C	= 26.9	
Ethyl alcohol (ethanol)	at 30°C	= 21.5	
H_2O + 50 vol% ethyl alcohol	at 30°C	= 27.5	
1000 g H_2O + 34 g NH_4OH	at 18°C	= 57.05	
1000 g H_2O + 17.7 g HCl	at 20°C	= 65.75	
Liquid CO_2	at 20°C	= 5.0	
1000 g H_2O + 14 g NaOH	at 18°C	= 101.05	
1000 g H_2O + 6 g NaCl	at 20°C	= 82.55	

Surfactants are the generic name for surface-active agents that reduce the interfacial energy of materials in contact. Surfactants used with water have both hydrophobic ("water hating") and lipophilic ("oil loving") groups and are categorized by the ratio of each type of material or the Hydrophilic-Lipophilic Balance (HLB), with low HLB being the most oil-soluble. Table 12-6 lists some HLB ranges and the application.[60] They dissolve in water by virtue of their hydrophilic groups and lower the surface energy of water to about 30 mJ/m^2. The surfactant collects at the interface between immiscible substances, such as oil and water, and lower the interfacial energy. Surfactants should only be used in de-ionized water. The correct formulation of surfactants in water can result in the emulsify or may "split-out" oils. Emulsification results in a suspension of the oil in water while splitting-out results in the oil segregating on the surface. Splitting-out has the advantage that the oil can be skimmed from the surface and the surfactant is available for further cleaning.

Table 12-6. Hydrophilic-Lipophilic Balance (HLB) Ranges and Applications

HLB value	Application
3.5–6	Water-in-oil emulsifier
7–9	Wetting agent
8–18	Oil–in-water emulsion
13–15	Detergent
15–18	Solubilizer

In solutions, pH adjusters are used to aid in the cleaning action. Generally it is found that basic solutions clean better than acidic solutions if chemical etching is not involved. The pH of the cleaning solution is often adjusted to be basic, using ammonia or ammonium hydroxide.

Chelating agents (sequestering agents) keep the normally insoluble phosphates, that are formed in hard water detergent cleaning, in solution. Glass cleaning solutions use chelating agents such as ethylene diamine tetraacetic acid (EDTA) and citric acid with salts containing hydroxyl and amine substitutes.

Deflocculants are chemicals that are added to solutions to help maintain the dispersion of contaminants in the cleaning medium. Deflocculants can be anionic or cationic surfactants or may be inorganic salts such as alkali phosphates. These materials will leave a residue on the surface if allowed to dry and will form insoluble phosphates if used in "hard" water.

Corrosion inhibitors are added to surfaces where the clean surface will react with the ambient in an undesirable way. For example, after cleaning tool steel, "flash rust" will form on the surface if a corrosion inhibitor is not added to the surface. Corrosion inhibitors can operate by adsorption of a molecular species on the surface to prevent oxidation or by forming a protective barrier that excludes oxygen from the surface.

12.3.4 Reactive Cleaning

Reactive cleaning uses liquids, gases, vapors, or plasmas to react with the contaminant to form a volatile or soluble reaction product. If nonvolatile products result from the reaction (e.g., silicone oil with oxygen to form silica) then a residue is left on the surface.

Oxidative Cleaning—Fluids

Reactive cleaning liquids are often oxidizing solutions. Many acid-based systems can be used as oxidants. One system commonly used in the semiconductor industry is the piranha solution. The piranha solution is hot (50°C) concentrated (98%) sulfuric acid plus ammonium persulfate.[61] The addition of the solid ammonium persulfate to the hot sulfuric acid produces peroxydisulfuric acid which reacts with water to form H_2SO_5 (Caro's acid), which further decomposes to form free atomic oxygen. The ammonium persulfate should be added just prior to the immersion of the substrate into the solution. The effectiveness of this oxidation technique can be shown by first placing a piece of paper in the hot sulfuric acid where it is carbonized, then adding the ammonium persulfate and watching the carbon disappear. This treatment is sometimes followed by a brief dip in a 10:1 solution of water and HF or immersion for 20 minutes in a hot solution of hydrogen peroxide and ammonium hydroxide in the ratio H_2O:H_2O_2 (30%):NH_4OH (29%) at 80°C. Another similar oxidizing solution uses stabilized sulfuric acid-hydrogen peroxide. Diaphragm

pumps, where all surfaces in contact with the fluid are made of Teflon™, are used to circulate the hot oxidizing fluids.

A hot chromic-sulfuric acid cleaning solution[62] prepared from potassium dichromate and sulfuric acid provides free oxygen for cleaning but has a tendency to leave residues and the surface must be rinsed very thoroughly. Disposal of the waste material is also a problem.

$$K_2Cr_2O_7 + 4H_2SO_4 \longrightarrow K_2SO_4 + Cr_2(SO_4)_3 + 4H_2O + 3O$$

Nitric acid can also be used as the oxidizing agent. Nitric acid with hydrofluoric acid is used to oxidize/etch surfaces such as silicon.[63] Nitric acid together with an oxide etchant such as hydrofluoric acid or ammonium bifluoride, can be used to simultaneously oxidize and etch oxidizable material such as the silicon in aluminum alloys.

Hydrogen peroxide (H_2O_2) is a good oxidizing solution for cleaning glass.[64] Often boiling 30% unstabilized H_2O_2 is used. Hydrogen peroxide is often stabilized, which reduces the release of free oxygen. Unstabilized H_2O_2 must be stored in a refrigerator to slow decomposition. Hydrogen peroxide is sometimes used with ammonium hydroxide, to increase the complexing of surface contaminants, and is used at a ratio of:

8 (30% H_2O_2):1 (NH_4OH):1 (H_2O)

However the decomposition rate of the H_2O_2 is greatly increased by combination with ammonium hydroxide.[65]

In cleaning silicon, the ammonical hydrogen peroxide solution may be followed by an acid rinse and this procedure is called the RCA cleaning procedure.[66]–[68] This solution has also been shown to be effective in removing particulate contamination from a surface.[69][70] The wettability of silicon in an alkaline solution is very dependent on the prior surface preparation (such as etching) and shows a profound hysteresis with the number of wetting cycles. A recent version of the RCA technique is called the modified RCA cleaning procedure[71]–[74] and is performed using the following steps:

1. H_2SO_4:H_20_2 at a ratio of 4:1
2. HF:DI water 1:100
3. NH_4OH:H_2O_2:DI water 1:1:5
4. HCl:H_2O_2:DI water 1:1:5
5. DI rinse

Oxidative cleaning can be performed using chlorine-containing chemicals. For example, a water slurry of sodium dichloroisocyanurate (i.e. swimming pool chlorine) which has 63% available chlorine, can be used to scrub an oxide surface to remove hydrocarbon contamination. This combines mechanical scrubbing with oxidation and improves the cleaning action.

Anodic oxidation in an electrolysis cell can be used to clean surfaces. For example, carbon fibers, which are formed by the pyrolysis of polymer fibers, have a weak surface layer. This layer can be removed by anodically oxidizing the surface in an electrolytic cell, followed by hydrogen firing.[75] This treatment increases the strength of the carbon fiber and improves the bond when the fiber is used as part of a composite material.

Oxidative Cleaning—Gaseous

Gaseous oxidation cleaning can be used on surfaces where surface oxidation is not a problem. Oxidation is usually accomplished using oxygen, chlorine, fluorine, ozone, or NO (nitric oxide) which creates volatile reaction products such as CO and CO_2.[76]

Reactive gas cleaning may use a reaction with a gas at high temperature to form a volatile material. High temperature air fire is an excellent way to clean surfaces that are not degraded by high temperature.[54] For example, alumina can be cleaned of hydrocarbons by heating to 1000°C in air. Self-cleaning kitchen ovens are cleaned by oxidation at about 405°C. Some care must be taken in furnace firing in that particulate generation, from the furnace liner, can be a source of undesirable particulates, and sodium from the insulating material may be an undesirable contaminant for semiconductor device fabrication.[77]

The use of oxidation by ozone (O_3) created by ultraviolet radiation (UV/Ozone cleaning) at atmospheric pressure and low temperature has greatly simplified the production, storage and maintenance of hydrocarbon-free surfaces.*[78]–[81] The UV is produced by a mercury vapor

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*The UV/O_3 cleaning process[69] was developed because of the need to clean very delicate quartz oscillators that had been fabricated by attaching the quartz to a flat plate with carnaba wax, then grounding and polishing to final dimensions. Any attempt to clean the quartz using physical contact caused breakage. The UV/O_3 cleaning technique provided a non-contacting way to clean the delicate quartz plates.

lamp in a quartz envelope so that both the 1849 Å and the 2537 Å radiation is transmitted. The short wavelength radiation causes bond scission in the hydrocarbon contaminants and generates ozone which reacts with carbon to form volatile CO and CO_2. The mercury lamps can be custom made to a variety of shapes for specific applications. Ozone adsorbs the UV so the substrates should be as close as possible to the UV source. UV radiation intensity should be maintained to about 1–10 milliwatts/cm^2 at the substrate surface. In the UV/O_3 chamber the air may be stagnant or flowing. If flowing air is used, the air should be filtered. The cabinet should be constructed of stainless steel with no polymers exposed to the ozone.

Typical exposure times for UV/O_3 cleaning are from a few minutes to remove a few monolayers of hydrocarbon contamination to hours or days or weeks for storage of cleaned surfaces. The UV/O_3 cleaning technique has the advantage that it can be used as a dry, in-line cleaning technique at atmospheric pressure.[82] The UV/O_3 cleaning technique is also useful for cleaning holes (vias) in surfaces.[83] In a correctly operating system, ozone can be detected by smell when the chamber is opened. The smell is similar to that of the air after a lightning storm and indicates that the ozone concentration is less than 10 ppmbv. Higher concentrations of ozone deaden the olfactory nerves and are harmful. The UV can also cause skin cancer and eye damage so the UV/O_3 cabinets should be constructed so that the UV lamp is turned off when the cabinet is opened. OSHA has set a limit of 100 ppbbv in the air over an 8-hour day, 6 days per week. At these levels, some irritation and discomfort will be noted by some people. A level of 10 ppbv is more reasonable. UV/Cl2 has been used to clean silicon surfaces[84] but the "activated" chlorine will rapidly attack stainless steel surfaces.*

High concentrations of ozone (10–20 %) are attained in ozone strippers. In these machines, ozone is created in a corona or arc discharge at atmospheric pressure. These strippers are used in the semiconductor industry to remove photoresists at rates of up to 1 micron per minute in a chamber heated to 300°C. It has been shown that UV assists in the stripping operation perhaps by forming radical sites in the resist.

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*The UV/O_3 cleaning process was used in a stainless steel chamber and it was found that the stainless steel was corroding. The source of corrosion was traced to chlorine in the air from "swamp coolers" used to cool the production area. The UV was dissociating the chlorine molecule and the "activated" chlorine was reacting with the stainless steel.

Hydrogen (Reduction) Cleaning

High temperature hydrogen or forming gas (90% N_2:10% H_2), can be used to remove hydrocarbon contamination from a surface by hydrogenating the material and making it more volatile. Hydrogen reduction of oxide layers can be used to clean surfaces in a furnace environment. Figure 2-16 shows the stability of a number of metal oxides at various temperatures and varying dew points (water contents) of the hydrogen. Depending on the dew point and the temperature, a hydrogen environment can either be reducing or oxidizing for many materials. Hydrogen cleaning can also change the surface chemistry. For example, hydrogen firing of a lead-containing glass produces a metallic lead surface by reducing the PbO to lead on the surface.

12.3.5 Reactive Plasma Cleaning and Etching

Reactive plasma cleaning[85][86] is a variation of reactive plasma etching (RPE)[87] that can be done in a plasma system separate from the deposition system. Reactive plasma cleaning uses a reactive species in the plasma to react with the surface to form a volatile species which leaves the surface at much lower temperatures than those used for reactive gas cleaning (Sec. 12.3.4). The additional requirement on reactive plasma cleaning is that it does not leave a residue. Oxygen (pure or from pure "medical" air), hydrogen (pure or as "forming gas")[88] are often used for plasma cleaning while fluorine (from SF_6, CF_4, CHF_3, C_2F_6, C_3F_8, or SF_6) and chlorine (from HCl, CCl_4, or BCl_3) are used for plasma etching. The reactive plasma cleaning/etching technique is typically specific and can be used to selectively remove the oxide from the surface and then have a low etch rate for the substrate material. Most metals are more easily etched using fluorine gas rather than with chlorine, since the metal fluorides are generally more volatile than the chlorides.[89] An exception is aluminum which is commonly etched using BCl_3.

Oxygen (or air) plasmas are very effective in removing hydrocarbons and absorbed water vapor from surfaces.[90][91] The reaction of the oxygen with carbon on the surface can be monitored using a mass spectrometer to monitor the CO and CO_2 that is produced.[92] Figure 12-4 shows a typical plasma cleaner where the plasma is generated by an rf discharge and the surfaces to be cleaned are in a "remote" or "downstream" location and not in the plasma generation region. Figure 12-5 shows the

processes that occur on a surface exposed to a plasma. The surface attains a potential (sheath potential) that is negative with respect to the plasma, and ions are accelerated from the plasma to the surface. For the case of a "cold plasma" which has low energy particles, this sheath potential will only be a few volts. When the plasma particles are more energetic or the electrons are accelerated to the surface, the sheath potential can be tens of volts. In addition to being bombarded by ions, the surface in contact with the plasma will be bombarded by "activated species," excited species, thermal species, and high energy photons (UV and, under some conditions, soft X-rays). Ions and excited species will release their energies of ionization or excitation when they impinge on the surface. For example, when a singly charged argon ion impinges on a surface, it will give up the kinetic energy it attained by acceleration through a potential and the ionization energy which is 15.7 eV.

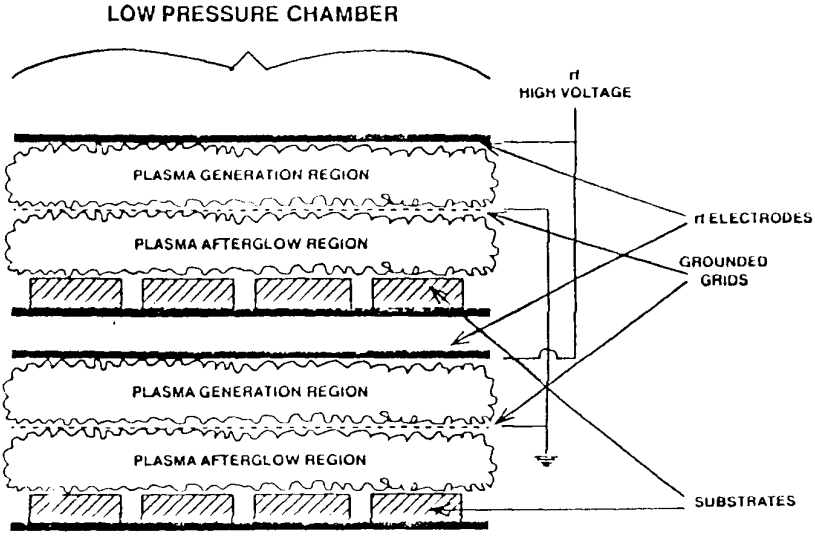


Figure 12-4. Plasma cleaner.

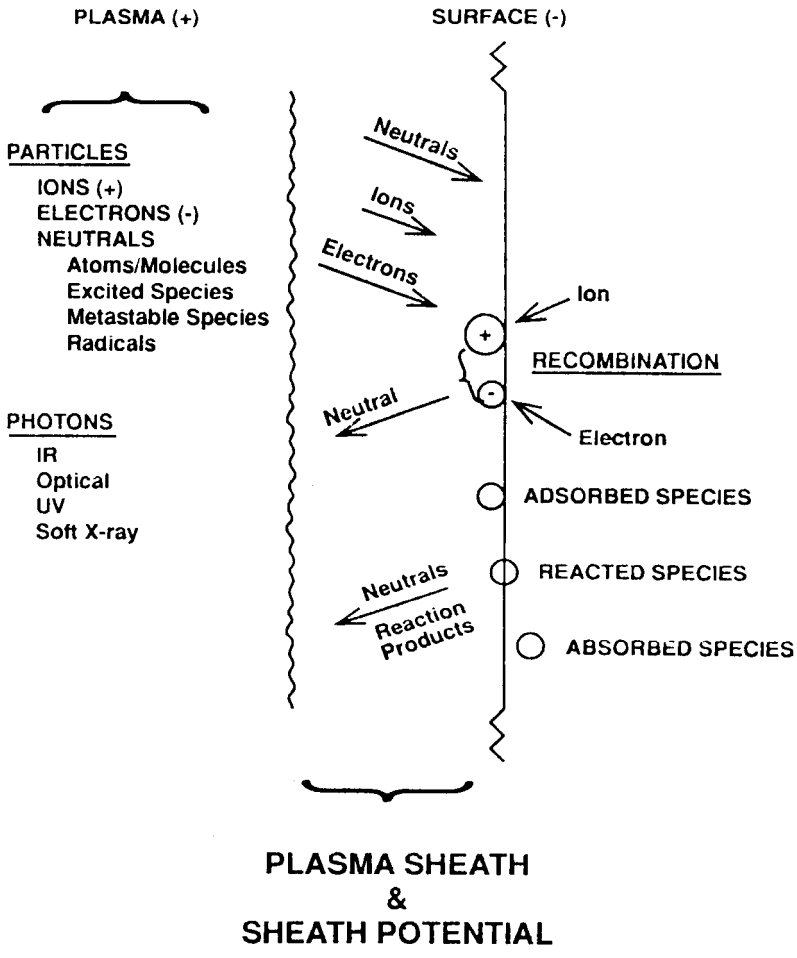


Figure 12-5. Plasma-surface interactions.

The plasma cleaner can have the substrate in the plasma generation region. A common configuration is when the substrate is placed on the driven electrode in a parallel-plate rf plasma system. When plasma cleaning or treating a surface it is important that the surface potential be uniform over the surface and that the plasma density be uniform over the surface. If these conditions are not met, non-uniform cleaning or treatment can occur. This is particularly important in the rf system, where if an insulating substrate does not completely cover the driven electrode the cleaning action is "shorted out" by the regions where the plasma is in

contact with the metal electrode. To overcome this problem a mask should be made of a dielectric material that completely covers the electrode with cut-outs for the substrates.*

Hydrogen plasmas can be used to remove hydrocarbon contamination when oxygen plasmas are unacceptable. This technique has been used to clean vacuum surfaces (stainless steel) in nuclear fusion reactors.**[93][94] Hydrogen plasma cleaning using a remote plasma cleaning reactor can reduce the temperature necessary for hydrogen reduction of oxides. Hydrogen plasmas have been shown to reduce the oxide on silicon at 500°C rather than the 900°C needed to reduce the oxide dry hydrogen firing.[95] Hydrogen plasmas have been used to clean metals[88][96][97] and semiconductor materials.[98][99]

External plasma cleaning generally relies on the naturally occurring sheath potential. In some cases a bias may be applied to the surface to increase the cleaning action. This increased bias can be accomplished by a DC bias on electrically conductive materials, an rf bias on insulating materials, or by increasing the sheath potential by accelerating electrons to the surface (Sec. 4.3). These techniques are generally used with *in situ* cleaning (Sec. 12.10).

Plasma etchers and strippers typically use more aggressive reactant gases such as chlorine or fluorine and are constructed to withstand corrosion and pump the particulates that are often formed in the etching and stripping process.[100]–[102]

An example of plasma etching is aluminum etching with boron trichloride (BCl_3).[103] The BCl_3 removes the aluminum oxide whereas other etchants such as Cl_2 or CCl_4 do not. Any water vapor in the etching

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*A person cleaning a dielectric substrate in an rf immersed system reported that the surface was being contaminated by the cleaning process. The dielectric substrate was not covering the whole electrode surface and material was being sputtered from the metal electrode and depositing on the substrate.

**In the TOKOMAK fusion technology, hydrogen plasma cleaning is used to clean the vacuum vessel. Typically a one day cleaning would bring the CO level down to the prescribed value. In one case it took over a week. After the fusion experiments had been performed, the vessel was opened and the residue from a plastic glove was found in the bottom of the vessel. The hydrogen plasma had completely volatilized the glove.

system will react with the BCl_3 to form particles of B_2O_3 which can clog the pumping system. When plasma etching is a copper-containing aluminum alloy, a copper chloride ($CuCl_2$) residue ("smut") is left on the surface which can be volatilized by heating to above 200 ^{0}C.

Often mixtures of gases are used for etching and cleaning. Oxygen is often added to the fluorine plasma to promote the formation of atomic fluorine and to oxidize the surface and thus increase the etch rate. One of the most common gas mixtures used to etch silicon is 96% CF_4 with 4% O_2. A mixture of HF and H_2O can be used to removed SiO_x from silicon.[104] Helium is often added to dilute the mixture and to increase the thermal conductivity of the plasma thus reducing the temperature rise of the substrate during etching. Numerous gases and gas mixtures are available for RPE.[89]

Etching and cleaning with compound gases should be used with caution since the decomposition products (B, C) can react with or deposit on the surface, thereby changing the chemical composition or contaminating the surface.[105] For example, when using a carbon containing chemical, (e.g. CCl_4 or CF_3) in the plasma, a residual carbon contaminate often remains.[85] Exposure to reactive plasmas can leave a reacted/chemisorbed layer of halogen species. This layer can be very important to the sensitization of the surface to atomic nucleation or the wetability of organic species to a surface. Reactive plasma etching of silicon in CF_4 plasmas has been reported to create a very thin fluoride layer that passivates the semiconductor surface to oxidation.

12.4 APPLICATION OF FLUIDS

Fluids are often used in cleaning processes. Fluid baths should be continuously filtered and monitored so as to replace or replenish the active ingredients as they are used or become contaminated. The particle content of the fluid can be continually monitored.[106] In cases of removing heavy contamination, the surface of the fluid can be "skimmed" as contaminants such as oils rise to the surface. This can be done by using "overflow" tanks or by skimming the surface with absorbent toweling. There are a number of ways to apply the fluids to the surface to be cleaned.

12.4.1 Soaking

Soaking (immersion) is a common cleaning technique for stubborn contaminants. Soaking involves extended times and therefore soaking has not been a desirable technique for production. This may change in the future when less aggressive cleaning chemicals must be used because of environmental concerns. Immersion of a surface in a stagnant solution is generally a poor technique since the contaminants that are taken into solution are concentrated near the surface and must diffuse away. Mechanical disturbance of the fluid can be done using agitation, wiping, brushing, or scrubbing in a fluid environment to loosen particles and aid in carrying contamination away from the surface. Care must be taken to ensure that any material that is used in a fluid does not produce particulates and is compatible with the fluid and surfaces it contacts. When using any mechanical rubbing, care should be taken to prevent contamination by abrasive transfer from the rubbing media—gentle pressure should be used. There are a variety of brush materials used in fluids including: polypropylene, polyvinyl alcohol (PVA), Teflon™ and Nylon™. If wiping or scrubbing with a cloth is used, care should be taken that the cloth is lint-free and desized by multiple washing before use. Special particulate-free sponge and cloth materials are available for wiping. In the semiconductor technology, mechanical scrubbing combined with high pressure fluid jets (2000–3000 psi) and spinning are standard cleaning procedures.

12.4.2 Agitation

Agitation is important in disrupting the stagnant fluid boundary layer that is present near surfaces. Mechanical agitation uses fixture movement to create currents near the surface. The fluid can be agitated by low and high pressure fluid flow or by bubbling gases through the fluid. In a fluid tank, this agitation can be accomplished using perforated pipes (sparagers) to distribute the fluid or gas being pumped through the system. Hydrosonic pressure waves directed toward the surfaces can also be used to disrupt the boundary layer.

Hydrosonic Cleaning

Hydrosonic cleaning utilizes hydrodynamically generated pressure waves to create agitation.[107] The hydrosonic agitation system is applicable to smooth flat surfaces, particularly for removing particles, but does not work well on configured surfaces where the surface is shadowed from the pressure wave. In some cases the shadowed areas collect contamination.

12.4.3 Vapor Condensation

Vapor cleaners (degreasers) operate by putting a cold part in the hot vapor above a liquid solvent contained in a "sump."[39][108][109] The solvent condenses on the surface and flows off into the sump. Since contaminants generally have vapor pressures less than the solvent, the vapor stays relatively clean. Cleaning action only occurs during the condensation process. When the part reaches a temperature at which the solvent does not condense, cleaning stops and the part should be removed. Parts should never be immersed in the sump fluid. Common solvents used in vapor degreasers are CFC-113 (trichlorotrifluroethane), TCA (methyl chloroform), TCE (trichloroethylene) and PERC (perchloroethylene). Azeotropes are mixtures of solvents that have the same composition in the vapor as in the fluid. For example a 50:50 mixture of CFC-113 with MEC (methylene chloride) gives the azeotrope Freon TMC™ which is used for metal degreasing. Fluid in the sump should be changed when it becomes contaminated.

Vapor degreasers have, in the past, been open to the atmosphere so solvent vapors escape into the atmosphere. A common mistake made with the old-style degreaser was to first clean the part using the spray wand then hold it in the vapor. Of course during spraying the part was heated and there was no condensation on the part when it was held in the vapor cloud. New designs for vapor condensation cleaning contain the vapor. Figure 12-2 shows a contained system where after the condensation ceases, the vapors are condensed on cooling coils before the system is opened and the parts taken out.

12.4.4 Spraying

Liquid spray pressures can be low, at less than a hundred psi, or high, at several thousand psi. Spraying parameters include the type of

fluid, pressure, angle-of-incidence, and volume of fluid. Sprays should be directed at an oblique angle to the surface. Spray systems often use copious amounts of material so the fluid should be recycled. The fluid should be monitored by residue analysis, and when it is contaminated above a given level it should be replaced. With increasing concern about solvent vapors, many of the newer solvent spray systems are self-contained with condensers to trap the solvent vapors (as shown in Fig. 12-2). Some systems allow the continuous purification of the solvents by distillation. Spray-cleaning is particularly applicable to fixturing and automation since the sprays can be made very directional. It should be noted that spraying can induce resonant vibrations that can dislodge parts from fixtures.

12.4.5 Ultrasonic Cleaning

Low frequency ultrasonic cleaning relies on the jetting action of collapsing cavitation bubbles in contact with a surface to provide a high pressure jet of fluid against the surface as shown in Fig. 12-6.[110]–[112] Ultrasonic cleaning is often a good way to remove loosely adhering particles after a grinding or abrasive procedure and can be used with solvents to remove adsorbed contaminants. Ultrasonic jetting is good for removal of large particles but less efficient as the particle size decreases into the submicron range.

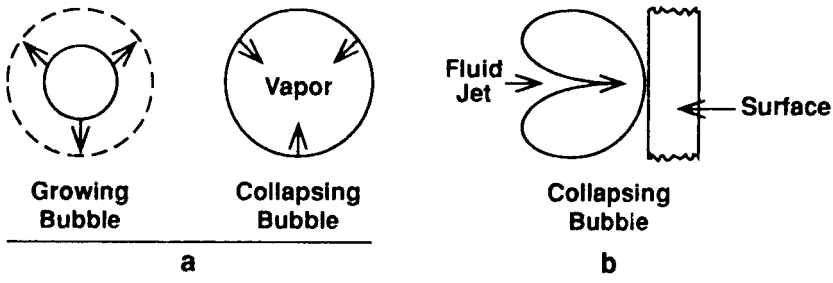


Figure 12-6. Ultrasonic cavitation: (*a*) bubble free in fluid, (*b*) bubble in contact with a surface.

The cavitation bubbles are formed by the tension portion of an ultrasonic wave in a fluid media and grow with time. The size that can be attained depends inversely on the frequency and the surface tension of the

fluid. High frequencies (>60 kHz) give smaller bubbles and a higher bubble density. The ultrasonic wave is produced by magnetostrictive or electrostrictive transducers(s) which can be attached to the fluid-containing tank walls or immersed in the fluid in the form of a probe that can concentrate the ultrasonic energy into a small area. Typically the transducers operate at 18–120 kHz, at an energy density of about 100 watts/gal of fluid. The ultrasonic cleaner size can be from 5 gallons for a small cleaner, up to very large systems using many transducers. The size of cavitation bubbles in the fluid depends on the vapor pressure, surface energy, and temperature of the fluid. For example, pure water at 60°C and 40 kHz has a maximum cavitation bubble size of about 100 microns if a surfactant is present, the bubble size is smaller due to the lowered surface energy. The jet pressure from the collapsing bubble can be as high as 300 psi. The cavitation jetting is more energetic for cooler media and when there are no gases in the bubble to hinder its collapse. Note: High power ultrasonic cavitation can fracture the surface of brittle materials and micro-roughen the surface of ductile materials. This can affect film growth and film adhesion.

The ultrasonic energy density decreases with distance from the transducer; therefore the cavitation energy is greatest near the transducer surface. Acoustic streaming results in an overall movement of fluid away from the transducer surface. If the transducers are mounted in the bottom of the tanks, this brings contaminants that have settled to the bottom of the tank up into the cleaning region. Therefore the cavitating fluid should be continuously filtered.

When using a fixed frequency transducer, there are nodes and antinodes formed (standing waves) in the fluid, which produce variations of cavitation energy with position. These standing wave patterns can be modified by reflection of the pressure waves from surfaces in the tank. This variation in cavitation with position can be overcome somewhat using swept-frequency generation. A typical system uses 40 kHz ± 2 kHz. If frequency sweeping is not used or there are large variations of cavitation energy with position, the parts should be moved from one region to another in the tank during cleaning. The ultrasonic frequencies are above the hearing range of the human ear and the audible noise that is heard from an ultrasonic cleaner is due to vibration of surfaces in the cleaner.

Variables in ultrasonic cleaning include:[113]–[115]

- Amplitude and frequency of pressure wave (energy density, standing wave pattern)

- Nature of the transducer fluid (density, viscosity, surface tension, vapor pressure)
- Nature of the cleaning fluid if different from the transducer media
- Surfaces in the transducer media that must transmit the pressure waves
- Flow and filtering of the cleaner fluid
- Temperature of the fluid
- Fluid contaminants such as water
- Gas content of the fluid
- Energy of cavitation implosion (temperature, pulse height of ultrasonic wave)
- Cavitation density changes with position in tank
- Cavitation density changes with time
- Shape of the pressure pulse
- Nature of the ultrasonic cycle train ("quiet time," "degas time," cycles per train)
- Geometry of the system and associated fixtures

The temperature of the transducer/cleaning media is important, not only to degas (exsorb gases) the fluids but to enhance cleaning and maximize cavitation. Some optimal temperatures for ultrasonic cleaning fluids are:

- Water with detergents, surfactants, etc., 130–150 ^{o}F
- CFC, 113–70–90 ^{o}F
- 1,1,1 trichloroethane, 100–110 ^{o}F
- Perchloroethylene, 180–190 ^{o}F

The intensity with which cavitation takes place depends on the properties of the fluid. The energy required to form a cavitation bubble in a liquid is proportional to the surface tension and the vapor pressure of the fluid. Thus, the higher the surface tension of the fluid, the greater the energy required to form a bubble, and the greater the energy released on collapse of the bubble. Water for instance, with its surface tension of about 70 dynes/cm, is difficult to cavitate. However with a surfactant, the surface energy can be lowered to 30 dynes/cm and cavitation is easier. Cavitation is enhanced with increasing temperature; however the jetting energy is

lessened at higher temperatures. Gases dissolved in the fluid enter the cavitation bubble and reduce the jetting energy, therefore fluids should be degassed for maximum cleaning effectiveness. Solvents in particular are susceptible to dissolved gases.

Ultrasonic erosion or deformation of aluminum foil or an aluminum metallized glass surface can be used to determine the cavitation power that a surface is exposed to in the ultrasonic cleaner. A general rule is that ultrasonic cavitation should generate 10 holes in a 1 x 2 inch area on aluminum foil of one mil thickness in 10 sec. The cavitation intensity can be studied by observing the cavitation damage on a series of aluminum foils with increasing thickness. The damage changes from hole-generation to dimpling to pitting, with foil thickness. The cavitation intensity of an ultrasonic cleaner should be plotted as a function of position with fixtures and substrates in position since reflections from surfaces can change the cavitation energy distribution. The cavitation pattern should be checked periodically, particularly if the fixturing is changed. Energy probes (watts per gallon) are available commercially to measure cavitation energy distribution in the tank but care must be taken that the pressure wave distribution is the same as when being used. Probes are useful for comparing the operation of a tank with time, loaded vs unloaded condition, and for comparing one tank to another. Some work has been done using sonoluminescence to visually monitor cavitation intensity.[116]

Fixturing is very important in ultrasonic cleaning to insure that all surfaces are cleaned. Generally, the total area of parts, in cm^2 should not exceed the volume of the tank, in cm^3. Parts should be separated and suspended with the surface to be cleaned parallel to the stress wave propagation direction. The parts must not trap gases which prevent wetting of the surface by the cavitating fluid. Metal or glass holding fixtures of small mass and an open structure should be used. Energy adsorbing materials such as polyethylene or fluoropolymers should not be used in fixturing since they adsorb the ultrasonic energy. Substrates should not be loosely placed in the bottom of a container which is suspended in the transducer fluid.

Often the cleaning fluid is filtered in a flowing system that exchanges 25–50% of its volume per minute. This is particularly desirable when the system is used continuously. An overflow tank system can be used to continuously remove contaminants that accumulate on the fluid surface. A cascade ultrasonic system with perhaps three stations of increasing solvent or rinse water purity can be used in the cleaning process.

Ultrasonic cleaning must be used with care since the jetting action can produce high pressures that cause erosion and introduce fractures in the surface of brittle materials. For example, in high power laser applications it has been shown that extended ultrasonic cleaning of glass surfaces increases the light scattering from the surfaces indicating surface damage. Ultrasonic agitation has been shown to create particles by erosion of the container surface. The erosion of stainless steel creates 500 times as many particles as the erosion of Pyrex™ glass containers. In all cases studied, particles of the container material were produced on prolonged use. Resonance effects may also mechanically damage devices in an ultrasonic cleaner.[117] Ultrasonic cavitation can also be a source of pitting and the loss of adhesion of thin films.[118] Surface damage can be controlled by adjusting the energy density of the cavitation and/or controlling the time of application.

Ultrasonic probes are available which allow directing the ultrasonic pulses to a small area. It is claimed that the probes provide ten times the cleaning power on an area than is available from an ultrasonic cleaner. These probes can be used by themselves or in conjunction with an ultrasonic cleaner.

12.4.6 Megasonic Cleaning

High frequency (>400 kHz) ultrasonic cleaning does not cause cavitation. Instead, the action consists of a train of wave fronts that sweep across a smooth surface producing disruption of the viscous boundary layers on the substrate surface by viscous drag. The resulting pressure is less than 50 psi and does not hurt fragile surfaces. High frequency transducers can be focused to restrict the area of impact and allow lateral fluid flow from the area of concentration.

Megasonic cleaning utilizes high frequency (850–900 kHz) transducers to produce non-cavitating pressure waves. The megasonic agitation system is applicable to smooth surfaces, particularly for removing particles, but does not work well on configured surfaces where the surface is shadowed from the pressure wave. The megasonic cleaning system is widely used to clean silicon wafers.[119]–[121]

12.4.7 Wipe-Clean

In some cases the surface can not be immersed in a fluid and must be cleaned by wiping.[122] Wiping with a fluid should be done with a moist lint-free cloth or sponge which has no extractables when in contact with the wiping-fluid. The wiping motion should be a rolling motion such that contamination that is picked-up does not come into contact with the surface as wiping proceeds.

12.5 REMOVAL OF PARTICULATE CONTAMINATION

Particulate contamination (including surface inclusions and irregularities) are a major source of pinholes in deposited films (Fig. 9-1). Particulates can be removed by the techniques discussed previously but can present special problems for cleaning. The ability to remove particles from a surface depends on the size, shape, and composition of the particle as well as the surface to which it adheres.[120][123]–[125] Particulate contamination can be removed by several mechanisms.

12.5.1 Blow-Off

Blow-off techniques have the advantage that they can be done after the substrates have been placed in fixtures and even in the deposition system. The best means of blow-off is to use filtered gas from a liquid nitrogen tank. The gas is filtered with a 0.2 micron or smaller filter in the nozzle. Ionized gas should be used when blowing-off insulator/organic surfaces to prevent electrostatic charge buildup on the insulator surface. A radioactive or electrostatic source in the nozzle allows ionization of the gas (Sec. 12.7.1).

Blow-off of particulates is often done with dusters using canned pressurized gases, or liquids that have a high vapor pressure at room temperature. One common duster, used before EPA restrictions on CFCs was dichlorodifluoromethane (DuPont Freon™ 12 -CCl_2F_2, boiling point = -30°C) which liquefies under pressure. Residuals from the blow-off gases should be checked, particularly with the spray can in the inverted position where liquid sprays-out instead of vapor.

12.5.2 Mechanical Disturbance

Removal of particulate contaminants, particularly small particles, from a surface is best done by mechanical disturbance in a flowing fluid environment.[126] The mechanical disturbance should be done in a fluid environment containing detergents and wetting agents and the fluid should be continually filtered. Dry or wet brushing is often used for particle removal. Camelhair and mohair are used for dry brushing. Polyvinyl-alcohol,[127] polypropylene, Teflon™, and Nylon™ are used for wet brushing. Mechanical disturbance is often combined with high pressure fluid jets (2000–3000 psi) as a standard cleaning procedure in the semiconductor industry.

Another mechanical particle removal technique is the use of high purity carbon dioxide "snow" formed by adiabatic cooling from a gaseous carbon dioxide cylinder through a small orifice.[128]–[130] The snow is entrained in the high velocity gas stream and mechanically scrubs the particles from the surface without leaving residuals or harming the surface, if the CO_2 gas is pure. This technique is also reported to remove fingerprints and silicone oil from silicon wafers and to be as effective as solvent cleaning for the removal of hydrocarbons in many cases.[131] A major processing variable is the purity of the compressed CO_2 gas. One problem that can be encountered with CO_2 spray cleaning is electrostatic charging of dielectric substrates.[132] Argon and nitrogen particles, which can be formed by cryogenically cooling the gas to form an aerosol, can be used to scrub submicron particles from a surface.[133]

12.5.3 Fluid Spraying

Generally high pressure (1000–2000 psi) fluid sprays are effective for removing large particles but are not effective on submicron sized particles.[126] Small abrasive particles, such as CeO, can be suspended in the fluid and aid in the cleaning action.[11]

12.5.4 Ultrasonic and Megasonic Cleaning

The jetting action of ultrasonic cleaning can be used to knock particulates from surfaces. Ultrasonic cleaning is not very effective in removing submicron-sized particles though higher frequencies (>60kHz)

are more effective than lower frequencies (20–40 kHz). The fluid drag associated with a pressure wave moving over a smooth surface in megasonic cleaning creates turbulence that knocks particles loose from the surface. If the surface is not smooth, particles can accumulate in depressions on the surface.

12.5.5 Flow-Off

Particles that are on the surface of a water-film on the surface can be removed by vapor condensation and flow-off during the drying cycle.[134]

12.5.6 Strippable Coatings

Particles can be removed from surfaces by covering the surface with a liquid polymer, allowing it to solidify, then mechanically stripping (peeling) the polymer from the surface. This technique is used by the optics industry to remove particles from mirror surfaces and protect surfaces from abrasion during assembly,[135] and in silicon technology to remove particulates from silicon wafers.[136] There are many types of "strip coats," each coating leaves different residues on stripping and have differing corrosion compatibility with surfaces. Hydrocarbon residues left by strippable coatings can be removed by oxidation techniques.

12.6 RINSING

After any wet cleaning process the surface should be thoroughly rinsed in pure or ultrapure liquid, usually water, before allowing to dry. This avoids leaving residues on the surface. A common rinsing technique is to use successive rinses (cascading rinsing) in pure or ultrapure water until the rinse water retains a high resistivity (e.g., >12 megohm). This is called "rinse to resistivity." Figure 12-7 shows a cascade rinsing system. A problem can be the "dragout" of one fluid with the part which then contaminates the subsequent fluid tank. For the beginning rinse, a sheeting agent can be added that lowers the surface tension of the water and aids in flowing the rinse water off the surface. After rinsing, the surface should be dried as quickly as possible since the residual water film on the surface will cause particles to stick to the surface and on drying the particles will adhere very tenaciously.

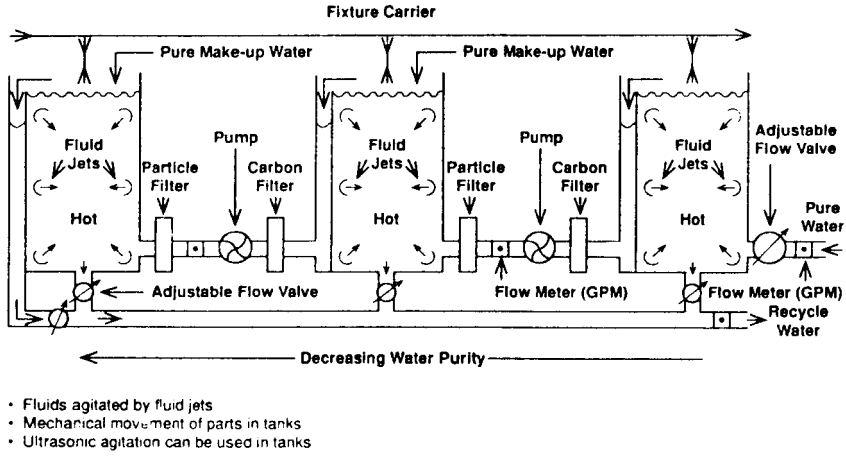


Figure 12-7. Cascade (counterflow) rinsing system.

12.6.1 Hard Water and Soft Water

Hard water contains metal ions, such as iron, calcium, manganese and magnesium, which can form water-insoluble salts when used with cleaning solutions and leaves a residue when evaporated. Soft-water is water that is relatively free of metal ion that form water-insoluble salts. A type of soft water is produced in a "water softener" by exchanging the ions that can form insoluble salts with sodium ions from sodium chloride (NaCl). The NaCl is water soluble however it will leave a residue when the water is evaporated. After using soft water for rinsing, the surface should be rinsed with pure or ultrapure water for the best residue-free surface.

12.6.2 Pure and Ultrapure Water

A material common to nearly all cleaning processes is water (H_2O). Contaminants that can be present in water are: ionic atoms and molecules, organic molecules, biological agents, and particulates. All of these can leave a residue when the water is evaporated. The type and amount of contaminants in the water depends on the source of the water and can vary with time.

Ultrapure (or semiconductor grade) water has all of the contaminants reduced to a very low level to prevent the deposit of residues when evaporated.[137] Ultrapure water is often called de-ionized water (DI water) because the most commonly measured contaminant is the ionic content of the water; however, care should be used in specifying DI water since it can contain appreciable non-ionic contamination. It is better to specify ultrapure water. To make ultrapure water, ions are removed from the water by ion exchange resins which remove ions by exchanging H^+ for cations and OH^- for anions. These resins must be replaced periodically. In some cases, particularly when high volumes of water are required, the ion exchange resin columns are preceded by a water softener or reverse osmosis system which increases the life of the exchange resins. Reverse osmosis (RO) uses a semipermeable membrane (pore size of 10^{-3} to 10^{-4} microns) which rejects salts, dissolved solids (90–98%) and organics (99%), but does require 400 to 600 psi feedwater and about 60% of the water is flushed away and does not enter the purification train.[138]

The ultrapure water is filtered through activated charcoal filters to remove organics and inert mechanical filters to remove particulates and biological agents. Mechanical filters should be made of a fluoropolymer such a Teflon™. Filters be staged with larger to smaller pore size and should have a final pore size of 0.2 microns. The filters remove biological agents that can grow on the filters. These biological agents should be killed using ultraviolet light or ozone dissolved in the water.

Spontaneous dissociation of the water molecule to OH^- and H^+ limits the resistivity of water to 18.2 megohms between electrodes spaced one centimeter apart (18.2 megohm-cm) at room temperature. This is equivalent to about 5 parts per billion (ppb) of NaCl. Electrical conductivity measurements do not measure the organic, particulate, nor biological contamination and other analysis techniques must be used to measure these impurities. In cleaning, the surface should be rinsed until the rinse water attains a specified resistivity (e.g., 5 megohm-cm, 10 megohm-cm, 15 megohm-cm, etc.) and this process is called "rinse-to-resistivity." If ultrapure water is exposed to the atmosphere it will absorb CO_2 forming carbonic acid (H_2CO_3) which will disassociate and decrease the electrical resistivity.

Specifications for ultrapure water can be as stringent as:

- Resistivity—18 megohm-cm continuous at 25°C
- Particle count—less than 500 particles (0.5 microns or larger) per liter

- Bacteria count—less than one colony (cultured 48 hours) per cc
- Organics—less than one part per million (ppm)

Particle content can be measured by light scattering. Organics can be determined by evaporation and residue analysis. Care must be taken that the ultrapure water is not contaminated in the water storage and distribution system so the analysis should be made on samples taken at the point-of-use.

Ultrapure water should be produce in quantities that satisfy the continuous and peak-level use requirements. High volumes of ultrapure water are made by:

- Pretreatment—pH adjustment, flocculation, filtration
- Reverse osmosis—removes most contaminants
- Degasification—removes dissolved CO_2
- Ion exchange (anion & cation)—removes ionic contaminants
- Absorption materials (activated carbon)—remove organics
- Filtration—removes particulates and biological matter
- Ultraviolet radiation or ozone[139] bubbling—kills biological agents on the filters
- Point-of-use filtration—0.2 micron filter pore size

Figure 12-8 shows one arrangement for producing high volumes of ultrapure water. Slightly contaminated water can be recycled ("polished") and reused. Smaller amounts of ultrapure water can be prepared by the same process steps beginning with the ion exchange process. Triple distilled water can also be used but it is relatively expensive.

Ultrapure water should be stored and distributed in materials which contain no extractable materials and do not support the growth of biological agents. The best container material is a fluoropolymer such as Teflon™ or HALAR™. High density polyethylene and polyethylene terephtalate (PET) can be used for storing ultrapure water. Low density polyethylene is porous and should not be used. Unplasticized polyvinyl chloride (uPVC) piping, or equivalent, should be used to distribute ultrapure water. The uPVC should be heat bonded or thermal welded instead of using glue bonding. Metal should be avoided since the ultrapure water will take metal ions into solution. Common chemical laboratory tubing such as Tygon™ should not be used since it has a high content of leachable polymers. In distribution systems, the water should be continuously

flowing or allowed to flow before use. It is not uncommon for the distribution system to become contaminated with biological agents which are then difficult to remove.* Ultrapure water should be heated by Teflon™-coated heaters. It should never come into contact with metal surfaces.

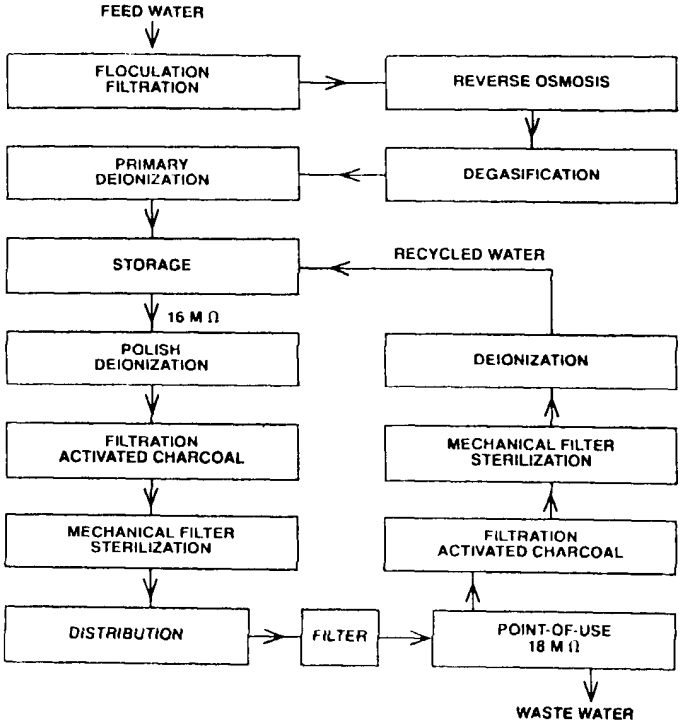


Figure 12-8. Production of ultrapure water.

The particle content of the fluid can be monitored in the distribution system.[140] Ultrapure water can leach silicates from soft glass—this was the source of "polywater" that was studied as a new form of water in

*I heard of a case where the ultrapure water distribution system became contaminated with biological agents ("wee beasties"). The maintenance people knew how to solve the problem—they dumped pool chlorine in the water feed. It blew-up the ion exchange columns. In another case, the top of the storage tank was left uncovered and seagulls left their waste in the storage tank.

the 1960's and can form colloidal silica particles (10–20 nm diameter) in the water. Particles can be filtered from the water using filters made from hydrocarbon polymers such as polycarbonates, nylon, fluoropolymers or polyethersulfone. The filter pore size can be as small as 0.03 microns.

Pure water can be produced using reverse osmosis (RO) along with particle filtration using mechanical filters and organic filtration using activated carbon. Often, pure water is acceptable and costs less than ultrapure water.

In some cases, soft water can be used for most applications and pure or ultrapure water used for the final rinse. In a cleaning operation, surfaces should never be allowed to dry before a final rinse in ultrapure water. It is interesting to note that in semiconductor processing the ultrapure water costs as much as the chemicals that they are removing with the water.[141]

12.6.3 Surface Tension

Water is often used in conjunction with a wetting agent, such as alcohol, to lower the surface tension of the water (Table 12-5). For example, water has a surface energy of 73.05 dyne/cm while a water 50% isopropyl alcohol mixture has a surface energy of about 27 dyne/cm. The lower surface energy allows the water to penetrate into small pores and cracks and decreases the size of stable water droplets.

12.7 DRYING, OUTGASSING, AND OUTDIFFUSION

12.7.1 Drying

Drying is the vaporization of water or other fluid adsorbed on the surface or absorbed in the bulk. Porous and rough surfaces retain fluids more readily than do smooth surfaces and are more difficult to dry since the fluids are trapped in capillaries. Oxide layers on metals are often porous and retain water molecules readily. Drying by removal or displacing the water has the advantage that when the water is removed it takes the bulk of the potential residues with it, whereas in vaporization or evaporative drying large amounts of fluid concentrates the residues and can give a "water spot" of residue. After fluid cleaning and rinsing, it is important to dry the surface quickly in order to prevent the water film from collecting particles.

Displacement drying uses anhydrous fluids, such as isopropyl alcohol (IPA),[142][134] anhydrous ethyl alcohol denatured with acetone or methanol, or a commercial drying agent such as a high vapor pressure Freon™ to displace the water from the surface and take it into solution. When the surface is removed from the fluid, the surface dries rapidly. Drying fluids should be residue-free and should be discarded or recycled as they take up water, either from the drying process or from the ambient. The water content of the drying fluid can be monitored by its specific gravity or by monitoring the infrared (IR) adsorption peak for water.

Many of the drying fluids used in the past have problems because of their Ozone Depleting Potential (ODP) or their Volatile Organic Components (VOCs). A potentially useful drying agent is acetone (CH_3COCH_3) which the EPA classified as being exempt from VOC regulations in 1995. Acetone is a good solvent for many contaminants, has a high evaporation rate and is miscible with water. Unfortunately it has a very low flash point (-4 ^oF) which means that it must be used with care. Acetone is easily contaminated so care must be taken that the acetone leaves no residue.

One of the best drying techniques is a "vapor dry" where the cold surface is immersed in the vapor above a heated anhydrous alcohol sump.[143][144] The cold surface condenses the alcohol vapor which flows off into the sump taking water and particulates with it. When the surface becomes hot, condensation ceases and the hot surface, when withdrawn, dries rapidly. The drying fluid can be enclosed and recycled (Fig. 12-6).[21]

Surfaces can be mechanically dried by shaking or spinning at a high velocity (>2000 rpm).[145][146] The equipment for high velocity spinning is common in the semiconductor industry where spinners are used to coat surfaces with photoresist. Spin drying tends to leave liquid along the outside edges of the substrate which can produce contamination in this area unless the surface is flushed with copious amounts of pure fluid. This technique leaves a thin film of water on the surface .

Surfaces can be blown dry using a low (<10,000 feet per minute [fpm]) or high (10,000–50,000 fpm) velocity dry gas stream. When blowing, a nozzle with a 0.2 micron or smaller particulate filter should be used in the nozzle. In addition, when drying insulator surfaces, the gas should be ionized to prevent charge build-up on the surface. The gas can be ionized with an electronic (corona), laser,[147] or nuclear (Polonium-210) ionizer. Electronic ionizers can arc and produce particulates. Nuclear ionizers are not sold anymore in the US due to restrictions on using radioactive materials but they can be leased and used with the same accountability as nuclear materials are used in medicine.

A high velocity jet of gas can be shaped to blow-off a moving surface. The jet is often shaped into a long thin configuration and this air knife is used to remove fluid from a moving surface such as a large glass plate. Exiting the air knife, the gas velocity can be as high as 35,000 fpm. The jet should impact the on-coming wet surface at about a 30° angle. At the trailing edge, a droplet will form and spread back over the surface when the jet is past so the fluid used should be ultrapure so as to leave no residue. The size of the water droplets can be reduced by decreasing the surface tension of the water by the addition of alcohol. This technique leaves a thin layer of water on the surface so subsequent heat drying may be necessary.

Hot gas drying or evaporative drying, uses the recirculation of hot dry, filtered air over the surface to promote evaporation. This drying technique has the problem of "water spotting" if the fluid is not ultrapure.

An interesting technique has been proposed for drying silicon wafers using the "Marangoni Principle."[148] The Marangoni Principle states that a flow will be induced in a liquid body where there are different surface tensions. If a surface is wetted by water and is slowly withdrawn from water, a meniscus will form. If a water soluble material, such as alcohol is present in the atmosphere above the water, the concentration of the alcohol will be greater in the meniscus than in the bulk of the water. This will create a difference in the surface tension of the water and the water/alcohol mixture will be pulled from the surface into the bulk of the water.

12.7.2 Outgassing

Volatile materials from the bulk of the material are removed by outgassing (Sec. 3.7). Since diffusion is required, the time to outgas a material may be very lengthy if the diffusion rate is slow and/or the diffusion distance is long. Generally metals primarily outgas hydrogen, particularly that taken up during acid cleaning, electropolishing, or electrodeposition. Glasses and ceramics do not outgas appreciably if they are fully-dense. Outgassing is especially important for polymers which absorb solvents and water,* and porous materials which wick-up solvents and water.

Problems were being encountered in the metallization of a styrene material from one supplier but not from another even though the compositions were supposed to be the same. By heating representative samples from the two suppliers and collecting the material vaporized from the surface on a KBr infrared window, FTIR showed that one material was outgassing significantly more vapors than was the other.

The usual technique used to outgas a material is to heat the material in a vacuum, at a temperature that does not degrade the material; this process is called vacuum baking. A common mistake is to vacuum bake the material for an insufficient time. Often many hours are necessary if the temperature is low and diffusion distances are long (Fig. 3-7). The time-temperature-vacuum conditions necessary to outgas the material can be determined by weight loss measurements using Thermal Gravametric Analysis (TGA), on the material. Microwave energy may be used to heat polar molecules such as water as long as there are no electrical conductors present. Microwave heating and drying may be more effective than conventional thermal heating.[149] It is often preferable to outgas a material prior to placing the materials in a deposition chamber rather than to outgas the material in the deposition system since outgassing can take appreciable time.

Some materials contain an almost unlimited supply of material that can outgas. For example brass, if heated in vacuum, will continually outgas zinc which will interfere with deposition on the brass surface. In this case, the brass must be sealed before coating. This is generally done with electroplated nickel or nickel-palladium (Sec. 2.6.4) . Polymers that outgas significantly can be coated with a basecoat which seals the surface.

12.7.3 Outdiffusion

Outdiffusion is the diffusion to the surface of material that is not volatilized. This material must be removed by surface cleaning techniques. For polymers, the material that is diffused to the surface can be low molecular weight constituents such as plasticizers. Brass outdiffuses zinc when heated and the zinc may or may not volatilize depending on the temperature. In many cases, the outdiffusing materials must be "sealed-in" by the application of a basecoat such as an epoxy on polymers or nickel on brass.[150] In some cases where there is a significant amount of material to be removed, the surface may have to be "outdiffused" and cleaned many times before an acceptable level of contamination is attained.

Porous surfaces present a problem for cleaning. If the contaminants are not cleaned from the pores they continually diffuse to the surface, contaminating the surface during processing. Porous materials are best cleaned by gaseous techniques where the reaction products are volatile. Cleaning of porous surfaces often requires raising the temperature to diffuse the contaminants to the free surface where they can be removed by solvents or reactive processes.

12.8 CLEANING LINES

A cleaning line is a sequence of procedures which compliment each other and results in a surface being cleaned to the desired level. The cleaning line may be manual, where the parts are transferred from one step to the next by an operator, or it may be automated, where the movement of the parts is automatic and pre-timed, or it may be a mixture of the two. In some cases, the parts to be cleaned may be held by special cleaning fixtures (racks) and the part must be placed on the holders ("racked") and removed from the rack after cleaning. In other situations, the cleaning rack is also used as the deposition fixture. This has the advantage that only the fixture has to be handled in transferring the parts from the cleaning line to the deposition system. A disadvantage is that the fixtures usually have to be stripped of deposited film before they can be used for cleaning again. In some cases, the cleaning line is integrated into the deposition line so there is no handling or storage between the cleaning sequence and the film deposition process. More commonly, however, cleaned parts are handled, stored, and transported either individually or in their fixture after the cleaning operation.

Figure 12-9 shows a typical cleaning line using aqueous alkaline cleaning applied both by immersion and spraying (both spray and immersion rinsing and hot air blow drying). Immersion cleaning with agitation and perhaps brushing, is often effective in removing exposed contaminants. Electrocleaning can be incorporated into the alkaline cleaning tank. If there is appreciable oil contamination, the first tank should be equipped with a "skimmer" or it should use overflow to skim the surface so that the parts are not extracted through an oil film when they are lifted out of the tank. Spray cleaning and rinsing has the advantage that "hideouts" such as cavities are continuously drained and refilled; whereas, in immersion cleaning, the cavities fill with fluid and the fluid can become stagnant in that region. Spray pressure should be as high as possible without causing damage to the substrates or knocking them loose from the rack. It may be desirable to mechanically move the parts in each step to aid in cleaning and draining.

It is important that the parts are not allowed to dry between steps. This means that the transfer between tanks should be as rapid as possible and the air above the tanks should be humid. In some cases, the cleaning line should be enclosed in a plenum to obtain better control of the environment surrounding the cleaning line. The plenum can be solid and have doors or a "soft-wall" to allow access to the cleaning line at any point. The soft-wall can be made of plastic sheets or strips. The plenum can be

slightly pressurized with clean filtered air to further control the cleaning environment.

Rinsing is important at several stages of cleaning. Rinsing between cleaning steps prevents the "drag-out" of chemicals from one cleaning step to the next. This rinsing step can often be done with "soft water" rather than pure or ultrapure water. The final rinse should be done with pure or ultrapure water. One key to effective rinsing is to use copious amounts of water. This means that some method of recycling of the rinse water is desirable.

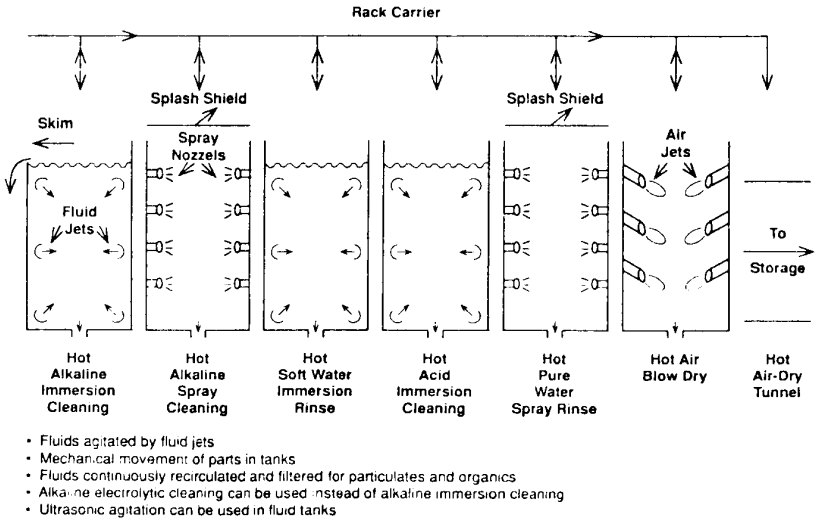


Figure 12-9. Typical cleaning line for non-rusting metal parts.

Ultrasonic agitation can be used in any of the fluid tanks. Ultrasonic power should be about 100 watts per gallon of fluid. For some materials, care must be taken when using ultrasonics since prolonged high-power ultrasonic cavitation can fracture the surface of brittle materials and deform, erode, and microroughen the surface of ductile materials. These surface features can then affect film growth and the resulting film adhesion.

The final step in the cleaning line is drying. Drying ensures that there is no significant amount of undesirable residue on the surface. In the cleaning line shown, drying is achieved by blow-off with hot air along with movement of the parts to allow draining from the hideouts. The parts can be further dried on their way to the storage or unracking area through a low-humidity hot drying tunnel. Drying can also be done using an enclosed vapor dryer (Fig 12-2).

After drying, the cleaned parts should be stored and transported in a manner that does not unduly recontaminate the parts.

12.9 HANDLING AND STORAGE/TRANSPORTATION

An integral, and often neglected, aspect of cleaning, is that of handling and storage before the next processing step or usage. Handling and storage during processing and after cleaning is a major source of recontamination. It is not unusual for a carefully cleaned substrate placed into a plastic bag to be recontaminated by the polymer—either by the volatile constituents or by abrasive transfer. The best procedure is to integrate the cleaning line with the deposition process so as to eliminate, to handle parts in fixtures, or minimize handling and storage. For example, in metallizing compact discs (CDs) the molded polycarbonate disc is taken directly from the molding machine into the deposition system where it is individually metallized with a cycle time of less than 3 seconds. Another example is the metallizing of mirrors where the glass is scrubbed, rinsed and dried just before being sent through an in-line metallizing system.

12.9.1 Handling

Often the best way to handle surfaces is to mount them in fixtures so that the active surfaces are not contacted directly. The next best technique is to use mechanical tools to hold and handle the surfaces. Often fixtures and tools can be designed that prevent surfaces from being touched in critical areas giving abrasive transfer between surfaces. Abrasive transfer can be a problem even with metal tools. For example, a clean oxide surface will easily transfer chromium from chromium-plated tools to the clean surface if there is abrasion. A protocol has to be established as to when and how to clean the tools, how to store the tools, how to use the tools, and what to do with them when they become contaminated.

Tools using suction to hold a surface ("vacuum tools") are often preferable to other types of holding tools since they minimize abrasive transfer of material by controlling the force between the surfaces. Clamping tools are available that limit the gripping force.

Gloves may be of a woven fabric or of a polymer film that is either molded to shape or heat welded from flat sheet. Polymer gloves for

general use are often powdered to make donning the gloves easier but for cleaning applications un-powdered gloves must be specified in order to avoid particulate contamination. Glove lengths can vary from wrist-length to elbow-length. Woven polyester glove liners that absorb moisture are available and make the wearing of gloves more comfortable.

There are a number of choices for polymer glove material including: latex rubber, nitrile rubber, vinyl, polyethylene, and fluorocarbon materials such as Teflon™ as well as polymer blends such as latex-nitrile-neoprene-natural rubber blends for use with acids. All glove material should have low-extractables for the chemicals that they might contact.[151] Vinyl gloves are comfortable and are often used in handling surfaces. A problem with the vinyl is that when it is in contact with alcohol, a common wipe-clean material and drying agent, the alcohol extracts phthalate plasticizers from the vinyl.* These extracted materials on the glove surface can then contaminate surfaces. Generally it is best not to have vinyl gloves in the cleaning area.

Unplasticized polyethylene gloves are compatible with alcohol and most cleaning chemicals, and are good gloves for clean handling. An advantage of the polyethylene gloves is that they are rather awkward and uncomfortable and operators will readily discard them when they are not required. Latex rubber gloves are often used in "suiting-up" for the clean room. A problem is that they are then used all day long, thereby transferring contamination from one place to another. When handling clean surfaces, an unplasticized polyethylene glove should be put on over the latex glove and then discarded when the handling is over. A disadvantage of the polymer gloves is that the soft polymer can be easily transferred to a clean surface by abrasive transfer. Abrasive transfer is dependent on the materials and the adhesion and friction between the surfaces.

Polymer gloves are slippery and it may be desirable to use fabric gloves such as de-sized and lint-free Nylon™ or Dacron™ woven fabric gloves when friction in handling is desirable or abrasive transfer from softer polymer gloves is a problem. Woven fabrics will wick oils from the skin to the glove surface, so polyethylene or latex gloves or finger cots

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*Demonstration: The effect of alcohol on vinyl can be demonstrated by putting the fingers of a vinyl glove in isopropyl alcohol for several hours. When removed and dried, the vinyl will be hard because of the extraction of the phthalates. Evaporation of the alcohol will leave a residue.

should be used under the fabric gloves. When handling hot surfaces, the gloves should be of a high-temperature fabric, such as Nomex® and not Nylon™ which will melt and fuse to the hot surface.

12.9.2 Storage/Transportation

Cleaned surfaces should be stored in a non-recontaminating environment. Often surfaces to be stored are held in clean fixtures to reduce the necessity for handling the surfaces directly. The fixtures must be compatible with the storage environment.

Passive Storage Environments

Passive storage environments are those which have been carefully cleaned and will not recontaminate the cleaned surfaces. A commonly used passive environment is a clean glass container such as a petri dish. Clean surfaces can be stored by wrapping them in a clean material. Wrapping the surfaces in clean, de-size nylon fabric covered by clean aluminum foil often works well. Often "white paper" has been bleached with chlorine and residual chlorine can corrode some materials. Unbleached paper or paper that has not been chlorine bleached should be used if corrosion is a problem. In some cases the surface should be wrapped in an anti-static material to avoid charge buildup on the surface. To avoid contaminants from the wrapping material, special cleanroom-compatible and antistatic wrapping and bagging materials are available. A simple method of passive storage is to place cleaned surfaces in contact with one another, this has been called "wafer bonding" in the semiconductor industry.[152]

Cleaned parts can be stored under liquids to exclude reactive gaseous agents. Metals stored in anhydrous liquids such as anhydrous alcohol or anhydrous acetone do not re-oxidize as rapidly as if they are exposed to the atmosphere. Storage of surfaces in degassed (boiled) water decreases the oxidation of the surface compared to water containing dissolved air.

In some cases, the surface condition can be preserved by covering the surface with a liquid polymer, allowing it to solidify and then mechanically stripping (peeling) the polymer from the surface when the surface is to be used. The strippable film technique is used by the optics industry to protect optical surfaces from abrasion and particulate contamination during assembly. Another method of using a strippable

film is to have a film that is easily removed by subsequent cleaning processes. For example, a molybdenum or carbon film can be deposited on a ceramic surface and then easily removed during a liquid oxidative cleaning process.

Active Storage Environments

Active storage environments are those where the contaminants are continually removed from the storage environment. Preferential hydrocarbon adsorption can be on freshly oxidized aluminum[153] or activated carbon. Hydrocarbon contaminants can be continually removed by having an oxidizing atmosphere to react with the hydrocarbons to form CO and CO_2. A UV/O3 cleaning cabinet provides such an environment. The UV/O_3 cleaning chamber is excellent for storing surfaces where surface oxidation is not a problem.

For some applications, moisture is the main contaminant to be considered. Moisture can be prevent from adsorbing or surfaces by keeping the surface warm in the storage environment. In some cases an actively desiccated environment is desirable. Common desiccants include: silica gel, phosphorous pentoxide (P_2O_5) and magnesium perchlorate ($Mg[ClO_4]_2$). Phosphorous pentoxide is probably the most effective desiccant material. It should be fused to reduce particle formation. Desiccants must be used with care since they tend to be friable and produce particulates. It is best to isolate the desiccants from the storage chamber by means of a particle filter. After prolonged use, desiccants must be exchanged or regenerated by heating.

Storage and Transportation Cabinets

In some cases storage, transportation and drying can be combined. For example, in cleaning and transporting large glass plates, a particle and vapor-free storage cabinet can be used. The cabinet should have heated, filtered air circulated through the cabinet to dry the plates and a UV/O3 ozone system to eliminate hydrocarbon contamination. It may be desirable to have an ionizer in the cabinet circulation to prevent electrostatic charge buildup on the glass if the air is very dry.

Sometime the cleaning area and the deposition area are separated and transportation from one to the other is necessary. For transportation the cabinet could be unplugged, moved, and then plugged-in. The cabinets should be loaded and unloaded in a clean area. Vibration from movement can knock particles free and the cabinets should be routinely checked for particulates.

12.10 EVALUATION AND MONITORING OF CLEANING

The best monitoring technique for cleaning is the ability of the process to provide surfaces that can be processed in an acceptable manner. The testing of a surface invariably results in contamination of the surface, so tested surfaces generally cannot be used for subsequent processing. In some cases witness sample surfaces can be tested for certain properties in order to determine surface conditions.[154][155] The *Military Standard MIL-STD-1246C (Product Cleanliness Levels and Contamination Control Program)* is a good specification for many cleaning programs.

12.10.1 Behavior and Appearance

The cleanliness of smooth surfaces can be determined during the rinse operation by observing the wetting and sheeting of water on the surface. Sheeting is the flow of the water over the surface as it drains, giving a smooth water surface. If there is hydrophobic contamination on the surface, the water will avoid that area and the sheet of water will "break-up." This test is often called the "water break" test.[62] This technique must be used with some care since if a hydrophilic contaminant, such as a soap residue, is present, the water will sheet over the contaminated area.

A common check on the cleanliness of a glass surface uses the contact angle of a liquid drop on the surface of the cleaned glass.[62][156]-[159] If the surface is clean, it has a high surface energy, and the liquid wets and spreads over the surface. In the case of water on a clean glass surface, the contact angle is less than 5° as measured with a contact angle goniometer.* This technique must be used with some care since, if a hydrophilic contaminant, such as a soap residue, is present, the contact angle may be low even though the surface is contaminated. For sensitive characterization of

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*As part of a specification for a cleaning process being transferred from the laboratory to production, it was specified that after cleaning, the glass surface must show a contact angle with water of <5°. The process engineer in the cleanroom found that they could not meet the specification and requested that the specification be changed. An investigation found that the exhaust of the mechanical pumps was near the air intake for the cleanroom and the filters were saturated with oil. The vapor contamination in the cleanroom was similar to that of a machine shop. The surface was recontaminated before they could make the contact angle measurement. The solution to the cleaning problem required a major overhaul of the cleanroom arrangement.

surface energies, liquids of various surface tensions can be used. Liquids of 30–70 dynes/cm (as per *ASTM D-2578*) are available. When using the dyne test, make sure that the dyne solutions do not dissolve surface layers or chemically react with the surface.[160] The dyne test can also be performed using marking pencils having various dyne-rated inks. Advancing and receding contact angle behavior can be studied using systems that add or remove fluid or by tilting the substrate.

A smooth clean surface will produce uniform nucleation of a vapor on the surface. A common test is to breath on the surface and look at the nucleation pattern. This is called the black-breath test.[54] For example, nucleation of water on the mirror in a shower room will show up the "swipes" where the mirror surface has not been cleaned very well. Nucleation uniformity over a large glass sheet can be evaluated by chilling the glass and then placing it in a high humidity. Nucleation uniformity over the whole surface can be evaluated by eye. Zinc nucleation has been used to study surface flaws in glass surfaces and the cleaning of glass surfaces.[161]

Absorption of a tracer material such as a fluorescent dye or radiochemical (e.g. Kr^{85}) can be used to detect the presence of many contaminants.*[66][67][162][163] Evaporative rate analysis (ERA) measures the evaporation rate of a radioactive-tagged material from a surface. Organic contaminates dissolved in the solution reduce the evaporation rate and, by calibration, the amount of organic present can be determined.[164] The MESERAN™ (Measurement and Evaluation of Surfaces by Evaporative Rate Analysis), from ERA Systems, Inc. is a commercially available ERA instrument. Fluorescent molecules can be observed at high resolution using a Laser Confocal Microscope (LCM).

A clean glass surface has a high coefficient of friction that can be detected by feel. If the surfaces are clean, there will be friction and the surface will feel sticky ("squeaky clean"). If the surface feels slick then it is probably contaminated. One type of friction test is the "marking test" where materials having various surface energies are rubbed on a surface.

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*Occasional problems were being encountered with the adhesion of the thin film metallization on the edges of a slip-cast alumina substrate. Adhesion tests near the center were always good but when a connector was slipped over the edge of the plate, adhesion failure was noted. Adsorption tests showed that there was more porosity near the edge than in the center on many samples. The supplier agreed that the material had not been properly fired. Improved acceptance tests put an end to the problem.

There is adhesion and abrasive transfer if the surface is of higher surface energy than the marking material. For example, indium will write on clean glass, and titanium or chromium will mark clean glass or alumina.

If surfaces are brought into contact they adhere. The coefficient of adhesion is the ratio of the contacting force to the strength of the bond and may be used as a measure of cleanliness.[1][165] The coefficient of adhesion can be used to monitor the recontamination rate (Fig. 12-1). A clean indium surface in contact with an oxide surface can be used to monitor surface cleanliness by the coefficient of adhesion.[166]

Often when looking at a surface, contamination appears as a haze.[167] This haze can be seen better under low-background-light conditions and with the illuminating light source at an oblique angle to the surface. This observation is a type of scatterometry.

12.10.2 Chemical Analysis

Extraction and analysis can be used to determine the type and amount of contaminant on a surface. Ionic contamination changes the electrical conductivity of ultrapure water and the conductivity change can easily be monitored after rinsing.[168] Non-ionic materials can be determined by residue analysis.[137] For monitoring hydrocarbons, commercial pyrolysis units are available that convert the carbon to CO_2, which is then analyzed by absolute coulometric detection.[169] Mass spectrometry can be used to identify atomic and molecular species in the gaseous or vapor state. An interesting mass spectrometric contamination identification technique uses a vacuum and heat to volatilize contaminants from a small area on a large-area surface using a vacuum probe that seals to the surface.[170]

Surface analytical spectroscopies such as Auger Electron Spectroscopy (AES), Ion Scattering Spectroscopy (ISS), Secondary Ion Mass Spectroscopy (SIMS) and X-ray Photoelectron Spectroscopy (XPS) (Sec. 2.4) can be used to characterize contamination levels on very small areas. Problems with the use of these techniques for cleaning evaluation is the small area analyzed and the potential for recontamination before the analysis can take place. When only a small area is analyzed, the true contamination condition of the total surface can be misjudged. The surface spectroscopies are quite useful in detecting and identifying heavy elemental contaminants and organic layers can be detected and identified using Fourier Transform InfraRed (FTIR) analysis.

It should be noted that any analytical technique using an electron bean for probing the surface can cause carbon deposition on the surface by decomposing residual hydrocarbon vapors in the system.[171]

12.10.3 Particle Detection

Particulate contamination on smooth surfaces such as polished silicon wafers can be detected by observing scattered light with an optical microscope[172]–[177] or by using a scanning laser microscope which integrates all the scattered light.[178] Laser light scattering is a sensitive technique and is capable of detecting particles as small as 0.2–0.15 microns in diameter with a probability of 90% to 50% respectively. Surface analytical techniques can be used to extend the detection of small particles.[179] Using angle-resolved light scattering, it is possible to obtain compositional and morphological data on the particle. Scanning interferometry can also be used to detect particles on smooth surfaces. Ultraviolet luminescence can be used to detect some types of particles.[180]

Particles on surfaces can be observed using Scanning Electron Microscopy (SEM), and in special cases Transmission Electron Microscopy (TEM). Compositional analysis of inorganic particles can be done using the SEM in the EDAX mode (SEM/EDAX) and by small area electron diffraction in the TEM.

Particles on rough surfaces can be detected by extraction techniques. For example, a strippable coating or tape can be applied and removed taking the particles with them. A particle count can then be made and the particles identified. Also the particles can be removed from the surface by wet cleaning, such as ultrasonic cleaning, then collected and identified.

12.11 *IN SITU* CLEANING

The surface can be cleaned in the deposition system by several means. This *in situ* cleaning is intended to remove the small amount of contamination that has developed since the external cleaning process was performed—**it is not intended to replace external cleaning!** One technique is to cleave or scrape the material to prepare a new surface under well controlled conditions.[3] To obtain an atomically-clean surface in vacuum can sometime take weeks.[5]

12.11.1 Plasma Cleaning

Plasmas can be used to clean surfaces in the deposition system in the same manner as they are used to condition vacuum surfaces (Sec. 3.11.3). In some PVD deposition systems which are not normally used with a plasma, a "glow bar" or "glow plate" is used as the cathodic or anodic electrode of a DC discharge to create the plasma. The larger the area of the surface, the better the plasma distribution in the system. Plasma cleaning can be done using an inert gas plasma or can use a plasma containing a reactive gaseous species to form a volatile reaction product from the interaction of the gaseous species and the surface species.

Ion Scrubbing

"Ion scrubbing" of a surface occurs when a surface, which is in contact with an inert gas plasma, develops a wall sheath and is bombarded by inert gas ions accelerated across this wall sheath as shown in Fig. 12-5. Generally the ion energy is too low to cause surface damage or physical sputtering, but is effective in the desorption of adsorbed surface contaminants such as water.

Reactive Plasma Cleaning/Etching

Reactive plasma cleaning/etching can be done in the deposition system in much the same way as was described in the "external" plasma cleaning (Sec. 12.3.5).[181]–[183] The surface in contact with a plasma containing reactive species develops a negative potential with respect to the plasma (self-bias). Ions, along with neutrals and "activated" species, of the reactive species bombard the surface producing volatile reaction product either with contaminants (cleaning) or the substrate material (etching) (Reactive Plasma Etching—RPE). The most common reactive gas used is oxygen or air. This type of plasma cleaning is reported to have been first used to clean optical surfaces by the Zeiss Company (Germany) in 1934[184] and was commonly used in early vacuum deposition processing.[185] In the early days, vacuum coaters would use the extinguishing of the glow as a vacuum indicator. Typically they would start their evaporation process 10 minutes after the glow went out.

Plasma cleaning can be used to clean surfaces without electronic damage of semiconductor materials.[186][187] In silicon technology, low energy hydrogen and argon plasmas, formed in an ECR discharge, can be used to clean the silicon surface with the hydrogen plasma clean giving the lesser electronic damage.[188] In configurations where the plasma is not in contact with the substrate surface, such as with planar magnetron sputtering, an auxiliary plasma can be generated near the substrate surface (Sec. 8.4).

To achieve high cleaning rates, high plasma densities are needed together with a large number of reactive species at reasonable plasma power densities. These plasma properties can be increased by increasing the electron-atom collision probability by:

- Short mean free paths (diode)—"high" pressures (<1 Torr)
- Auxiliary electron source (triode)—low pressures (0.01–0.2 Torr)
- Increased path length (magnetron)—very low pressures (<0.01 Torr)
- Microwave plasma excitation (ECR or other)

12.11.2 Reactive Ion Cleaning/Etching

In reactive ion cleaning/etching (RIE), energetic reactive-ion bombardment of the surface is used to add kinetic energy to the bombarding etching species. The ions are accelerated to the substrate under a high applied negative bias or under a high self-bias. In the case of conductive surfaces, a DC potential can be applied. In the case of electrically insulating surfaces, an rf or pulsed DC potential can be applied. In applying an rf bias, the surface to be cleaned does not have to be in direct contact with the electrode surface.[189]

It has been shown with RIE of silicon using chlorocarbon gases, such as CCl_4, that carbon residue limits the rate of etching. In RIE of silicon, the carbon residue that remains on the surface must be removed by a postdeposition treatment of low temperature oxygen annealing.[190] When etching oxides, or there is oxygen in the plasma, the oxygen prevents the formation of the carbon layer and higher etch rates result.[191] Typically, RIE introduces less surface damage in semiconductor materials than sputter etching, but more damage than RPE. RIE of silicon surfaces has been shown to roughen the surface by attacking reactive surface sites.

A major concern in any plasma process is to obtain a uniform plasma over the surface. Some plasma-generation configurations are more amenable to uniformity than are others. The magnetron configuration is one where plasma uniformity is difficult to obtain except in certain applications such as passing the substrate through the plasma of a planar magnetron. Another magnetron configuration uses electromagnetic field rotation over a silicon wafer surface to obtain uniform etching without substrate damage.[192]

In RPE and RIE, the gas density and flow pattern are important to etch/cleaning uniformity. Gas is typically introduced through a series of orifices or in some cases porous diffusers that are positioned to produce the best flow uniformity and plasma density. In high pressure reactors, where the electrode spacing is small, plasma uniformity is particularly difficult to obtain. The gas density and flow are often disrupted by fixturing and temperature variations in the system and these change when the internal geometry is changed.

The reactive etching/cleaning processes produce volatile species which may be deposited in other parts of the system where there are different plasma conditions. This may have a detrimental effect on the gas handling/pumping system and can be a source of particulates in the etching system.[193]

Reactive Cleaning in a Vacuum

The use of ion and neutral beams allow the cleaning/etching of a surface in a good vacuum environment. Energetic ion beams of reactive species can be used to clean/etch surfaces and the process is called Reactive Ion Beam Etching (RIBE).[194]–[196] Beams of uncharged radicals of reactive species (H, Cl, F) can be used to clean surfaces in vacuum.[196][197] The use of energetic inert gas ion beams to bombard a surface concurrently with a molecular beam of the etchant gas (Ion Beam Assisted Etching—IBAE) shows enhanced etching over either the inert ion bombardment (sputtering) or the molecular beam alone.[198][199] It has been shown that inert ion bombardment increases chemical reactivity at a surface although the mechanism is not well understood.[200]

12.11.3 Sputter Cleaning

Sputter cleaning uses physical sputtering (Ch. 6), not chemical reaction, to remove some of the surface layer, which includes the contaminates.[202]–[205] Sputter cleaning has been called the universal etch since conceptually everything can be removed by the sputtering process. However certain types of surface contamination, such as particles and inclusions of inorganics compounds, are very difficult to remove by sputtering because of their shape. This cleaning process can be easily integrated into the deposition process so as to allow no time for recontamination between the cleaning and the deposition process as is done in ion plating (Ch. 8). Sputter cleaning has been shown to produce detrimental surface damage on silicon surfaces.[206][207] It has been reported that energetic atom bombardment induces less electronic damage than does ion bombardment at the same energy.[208]

During sputter cleaning, the bombarding gas may become incorporated into the surface and subsequently released on heating.[209]–[212] The incorporated gas can cause loss of adhesion of films deposited on the bombarded surface. To avoid this problem, the substrate should be heated during bombardment or prior to film deposition to prevent or outgas gases included in the substrate surface. Sputtering from a plasma environment has the disadvantage that gaseous contamination in the plasma becomes activated and can react with the surface being cleaned;[204] also sputtered species can be returned to the surface by scattering (redeposition) and contaminate surface species can be recoil-implanted into the surface. Sometimes this makes sputter cleaning difficult.

Ion milling, where ion beam sputtering is used to remove surface material, can be done in a vacuum environment where the sputtered species are not redeposited on the substrate surface and gaseous contamination is rapidly pumped away.[213]

12.11.4 Laser Cleaning

Laser ablation (vaporization) uses very short pulses of high peak power laser irradiation to rapidly heat and vaporize thin layers of surface material under vacuum conditions (Sec. 5.3.5) and can be used to clean a surface.[214]–[216] Generally, UV (krypton-fluoride) lasers clean oxide surface most efficiently since the UV radiation is easily absorbed by the oxide.[217] Laser heating of silica, alumina and zinc oxide surfaces with a

CO_2 laser at 3–7 W/cm^2 is reported to produce the same surface condition as does heating to 400–1000°C.[218][219]

Particulates can be removed from a surface by using a laser to vaporize a thin layer of fluid that surrounds the particle on the surface. In one application, the substrate is heated by a KrF UV laser (0.248 micron wavelength);[220,221] in another, the fluid (water) is heated directly by a CO_2 IR laser (10.6 micron wavelength).[222]

12.11.5 Photodesorption

UV radiation can be used to thermally desorb surface species by photodesorption.[223][224] This technique is used to remove water vapor from surfaces in a vacuum system.

12.11.6 Electron Desorption

Electron bombardment can be used to desorb some surface contamination. However, electron bombardment of a hydrocarbon is likely to pyrolyse the hydrocarbon and form a carbonaceous layer on the surface.

12.12 CONTAMINATION OF THE FILM SURFACE

The contamination of the film surfaces after film deposition but before the next processing step or before use can be a concern.* The as-deposited film surface is clean and has a very reactive surface. In addition, it may have a very high surface area and be porous because of the growth of a columnar film morphology. This means that if the surface is contaminated it will be very difficult to clean. The surface should be protected and stored commensurate with its subsequent use (Sec. 12.8).

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*The web had been metallized and rewound and shipped to the "convertor" who makes the web into a product. The convertor found that he could not print on the metallized surface and the metallizer thought that there was something wrong with the deposition process. It was determined that the problem was the web material had a low molecular species which, on storage, contaminated the surface with a low energy contaminant that prevented printing.

12.13 SAFETY

Appropriate laboratory safety methods and procedures should be used at all times in the cleaning process.[225]–[227] The safety and hazardous nature of various chemicals can be found in the Merck Index. Various industrial organizations have formulated guidelines for the safe use of industrial chemicals. For instance, the Institute for Interconnecting and Packaging Electronic Circuits has issued a guideline entitled "*Guidelines for Chemical Handling Safety in Printed Board Manufacture" (IPC-CS-70)*. In the United States, the Federal Government (OSHA) establishes exposure limits for various toxic and carcinogenic chemicals. These limits should be strictly adhered to in the workplace. Table 12-7 shows some exposure limits. Reference should be made to current OSHA guidelines since they change frequently. Cleaning facilities should be designed with safety in mind.[228][229]

Chemical manufacturers and distributors are required to provide Material Safety Data Sheets (MSDSs) for all materials when shipped. OSHA has mandated that employees must be provided with this information and trained with respect to the hazards of the materials that they are using (*Hazard Communication Standard 29 CFR 1910.1200*).[230]

Table 12-7. Solvent Exposure Limits

Solvent	8-hr Time-Weighted Average (TWA) - ppm	Short-Term Exposure Limits (STEL) - ppm
Methylene chloride*	500	1000 max
Perchloro-ethylene*	25	—
Trichloro-ethylene*	50	200
1,1,1-trichloro-ethane	350	450

12.14 SUMMARY

12.14.1 Cleaning Metals

Gross contamination, such as oil films, should be removed by appropriate cleaning techniques. Except for gold, all metals will have a natural oxide layer. If the oxide is thick, it should be removed during the external cleaning process. A thin oxide can be removed by *in situ* cleaning. If an oxide layer can be tolerated, the metal may be cleaned by a oxidizing technique. *In situ* cleaning in the deposition system can be use to remove small amounts of recontamination and surface oxides.

12.14.2 Cleaning Glasses and Ceramics

Oxide glasses and ceramics can be cleaned by oxidizing techniques. If there is a heavy contaminate layer or if the oxidizing cleaning leaves a residue, the surface can be cleaned by a solvent or etching technique. In the future, the cleaning of glass for flat panel displays, where particle (>1 micron) contamination is a major concern, will require one of the most demanding cleaning procedures.

12.14.3 Cleaning Polymers

Polymers can best be cleaned using a solvent or detergent cleaning process. Often the polymer must be outgassed or coated with a basecoat to prevent outgassing and outdiffusion. The polymer surface may be activated by plasma treatment to aid improve film nucleation on the surface (Sec. 2.6.5).

FURTHER READING

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13

External Processing Environment

13.1 INTRODUCTION

The ambient environment is the laboratory or production environment in which the substrates, fixtures, vaporization sources, etc. are processed prior to insertion in the deposition chamber. This environment consists not only of the air but also processing gas and fluids, and surfaces which can come into contact with the substrate. This ambient environment always contains potential contaminants. The control of this environment is often necessary to insure process and product reproducibility. Cleaning should be done in an environment and with procedures that are compatible with the level of cleanliness desired. Reduction of contamination in the environment can range from very simple to very elaborate and costly procedures.

During cleaning, it is better if substrates are held in holding fixtures made of materials that can be easily cleaned and do not contain potentially contaminating materials such as the plasticizers on molded polymers. Glass, ceramics, hard metals, or un-plasticized polymers are used as fixturing materials. It is best if the fixtures do not touch areas of concern since "abrasive transfer" of clean materials in contact can result in contamination. The use of cleaning fixtures reduces the amount of touching of the critical surfaces by the operator during the cleaning process.

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13.2 REDUCTION OF CONTAMINATION

Clean surfaces are very reactive and easily recontaminated. Recontamination can occur from the adsorption of vapors, collection of particles, contact with other surfaces or reaction with reactive gases. Important aspects of cleaning are the conditions existing in the processing area, the handling of the surfaces, and storage of the cleaned part. Dust is a particular concern in many instances since particulates on the substrate surface will result in pinholes in the deposited film. Figure 12-1 shows the recontamination of a clean gold surface in a very clean environment, a typical cleanroom environment and in a "machine shop" environment as determined by coefficient of adhesion measurements between gold surfaces.[1] The recontamination is primarily by the adsorption of hydrocarbon vapors on the clean gold surfaces.

13.2.1 Elimination of Avoidable Contamination

Avoidable contaminants in the processing area include large and small particulates, some vapors, and some reactive gases such as chlorine. The least expensive action that should be taken to reduce contaminants in the processing area is to remove as many sources of contaminants as possible. This can mean good "housekeeping," separation of contaminant-producing processing from the cleaning area, elimination of particulate-producing materials, elimination of vapor-producing materials such as many molded plastics and vinyl coverings. Personnel doing the cleaning should not use particulate-producing products such as mascara or body powders.

Housekeeping

Particulate contamination in the ambient may be minimized by:

- Good housekeeping
- Minimizing dust and particulate generating activities and materials, e.g., cotton clothing/sloughing, skin/powder cosmetics, common paper, soldering fluxes, aerosols (liquid particles)
- Using low velocity air currents with little turbulence

- Eliminating electrostatic charging of insulator surfaces which attract particulates
- Mechanical, electronic and electrostatic air filtration

Housekeeping is aided by minimizing the amount of "things" in the area and keeping "things" in cabinets. Cabinets and furniture should be designed so that they can be easily cleaned and do not present areas of stagnate air flow where dust can accumulate and then be disturbed. For example, the top of cabinets can be extended to the ceiling so that dust doesn't accumulate on the top and people don't store things on top of the cabinets. The cabinets should either sit directly on the floor or should be high enough off the floor that cleaning under them is easy.

Construction, Materials, and Furniture

The construction and materials used in the clean areas are important. Materials such as short fiber cloth, carpeting, chair padding, etc. should be avoided. A very common problem is to use fiber-padded chairs that "puff-out" particles every time they are sat on. Acoustic tile is also a common source of particulates.

One of the major factors in the control of hydrocarbon vapors is the coverings of the furniture, walls, and floors.[2] Table 13-1 shows outgassing rates for materials used in clean rooms.[3] All surfaces should be compatible with "wipe-down" solvents such as alcohol or acetone/ methanol. Vinyl coverings and padding on chairs should be avoided since they are not compatible with alcohol.

Construction should be such that there are no "hide-outs" for contaminants. Examples are spaces under and on top of cabinets where particulates and dust can accumulate.* The clean area should not be cluttered with extraneous equipment and furniture and should be designed for easy cleaning. Furniture should be of solid material or padded with foam not fiber.

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*One of the first things to do in evaluating a cleaning area is to look under the furniture for "dust-balls" ("dust-bunnies"). The "white-glove" inspection is also useful.

Table 13-1. Typical Outgassing Rates of Construction Materials.[3]

Material	Typical outgassing rate (Torr liter/sec /cm^2)
316L stainless steel—baked 300°C/24 hr/inert atmosphere	0.000075 x 10^{-6}
316L electropolished stainless steel	0.0015
304 mill stainless steel	0.0120
Hard coat anodized aluminum sheet	0.2210
6061 mill aluminum sheet	3.12
HEPA filter paper	5.96
Fused epoxy powder coating	6.13
Chemical resistant polymer flooring	119.96
Acrylic latex paint	224.19
Oil-based enamel paint	248.55

Elimination of Vapors

Vapor contamination is generally not controlled in the processing environment except by ventilation, construction, and segregation of vapor-producing processes such as soldering, etching, electroplating, etc. from the clean area. Vapor-producing and aerosol-producing processes should be performed in ventilated work areas such as "chemical hoods." Some filter systems use activated carbon to filter organic vapors. Activated carbon is an amorphous material with a high surface area (500–1500 m^2/g). For use in gases, it has a pore size of 12–200 Å. Activated carbon has a high affinity for the absorption of organic molecules. It is better for adsorbing non-polar molecules than polar molecules. Catalytic agents (Cu, Ag, Cr) in the activated carbon can be added to improve the absorption of complex organic molecules and are used in gas mask filters.

13.2.2 "Containing" Contamination-Producing Sources

Another action that can be taken to reduce contamination is to contain contaminant-producing sources as much as feasible. Humans and their clothing shed large amounts of particulates that are "pumped out"

through the loose weave of the clothing as the person moves about. The use of head coverings, facial hair coverings and coats or coveralls ("bunny-suits") of tightly woven long-fiber cloth will contain the particulates somewhat. In particular hair and mouth should be covered since the head is often over the surface being processed.

13.2.3 Static Charge

Ions can be introduced into the work area from ionizers. These ions attach to airborne particulates which are then attracted to grounded surfaces.

Static charges on surfaces can be generated by movement, particularly if the air is very dry. This static charge can then attract airborne particulates. A humidity of about 40% is the most desirable for comfort and to minimize static charge buildup.

13.3 MATERIALS

Materials used for cleaning should be compatible with the cleaning level desired.[4,5] Their use can also be controlled by the application. For example, when handling heavy parts, fabric gloves should be used because of the higher friction that can be obtained and the reduced chances for abrasive transfer of contaminates.

13.3.1 Cloth, Paper, Foils, etc.

When weaving a fabric the threads are often coated with a lubricant called a sizing agent. The sizing is often polyethyene glycol which is water soluble and can be removed (i.e. desized) by multiple washing. Sodium silicate may also be used as a sizing and it is difficult to remove by washing. Cloth should be woven from long filament fibers so the ends will not break off creating particles (i.e. non-linting). Use, and multiple washing will break the filaments and the cloth will become more of a source of particles with use. Polyester is the preferred woven fabric for cleanroom use. Polyester fabric such as Dacron™ is more desirable than Nylon™ in that it is less absorbent, more wrinkle resistant and more opaque than Nylon™. The edges of cut cloth may be heat-sealed to reduce particle formation. Woven fabric can be overcoated with a plastic to make it more particle free.

Close-woven polyester cloth is a common material for clothing. The close weave prevents particles from escaping through the cloth during body motion. This close weave also means that the fabric does not "breath" water vapor very well and the clothing can be uncomfortable. Tyvek™ is a paper-like product which is widely used for cleanroom clothing. A special cloth made of porous Teflon™ sheeting laminated with woven fabric is called Goretex™. GoreTex™ is used as a breathable but non-wetting fabric. GoreTex™ is formed by rapidly stretching Teflon™ at 350°C. The resulting porosity looks like a pile of fishnet and has pores of about a micron in diameter. This fabric is especially useful as clothing since the pores are small enough to "breathe" water vapor but too small to let particulates escape through the fabric. Non-woven fabrics, such as spun-bonded polyolfins, are cheaper than woven fabrics but tend to abrade more easily than the woven fabrics and should not be used in particle-sensitive areas.

Common cellulose fiber paper will shed lint. The cellulose paper can be coated with a polymer to prevent linting and this type of paper should be used in the cleaning area. Carbon-lead pencils should not be used in the cleaning area since they produce particulates. White paper has been bleached and often has chlorine still in the paper. This chlorine can cause corrosion. Paper can also contain sulfur which can cause corrosion problems. Neutral pH paper both buffered and non-buffered is available from photography supply houses. Paper products can absorbed water vapor and corrosive gases from the environment and become a source of corrosive agents. Substrate surfaces should not be stored in contact with paper. Paper can be overcoated with a plastic to make it more particle free.

Most adhesives have corrosive components, generally chlorides. There are some neutral pH adhesives but generally they are not good adhesives. Neutral pH adhesives are available from photography supply houses.

Aluminum foil is often used in clean areas. Common aluminum foil, such as is bought in a grocery store, is coated with oil or wax and must be cleaned before use. Special UHV grade aluminum foil has no such surface contamination and can be used with minimal cleaning.

Polymers should be tested for "extractables" before use.[5] The amount of extractable material is determined by the formulation of the polymer mix. Molded plastics often have a high plasticizer content to make them more fluid for molding. These low-molecular-weight plasticizers migrate to the surface and contaminate the surface. In semiconductor processing, a relatively inert fluoropolymer (perfluoroalkoxy—PFA,

e.g. Teflon™ or Neoflon™) is often used for containers and holders but they can liberate corrosive fluorine compounds. Special treatments are used to reduce the extractable fluoride compounds from these materials.[6] Many polymers can absorbed water vapor and corrosive gases from the environment.

Various polymer web (sheet) materials are commonly used in cleaning and storage applications. PVDC (copolymer of vinylidene chlorine and vinyl chloride), PVC (polyvinyl chloride) and PE (polyethylene) are the most common. PDVC and PVC generally contain plasticizers and can contaminate clean surfaces. Polyvinyl chloride can breakdown in the presence of water and form hydrochloric acid. Unplasticized PE (uPE) is the most desirable wrap material. Polymer wrap material can have antistatic coatings. Often these coatings are ionic materials that pick up moisture from the air to form an electrolyte on the surface. This electrolyte material is often corrosive. Polymers may be made conductive by the incorporation of carbon in the bulk of the material. This provides an noncorrosive antistatic material. Polymers can also have other coatings to prevent "cling," to raise or lower the friction, for abrasion resistance, etc., and such coatings should be known and understood. Polymer materials that may also be used for wrap materials include: fluoropolymers (e.g. Teflon™), unplasticized polyester (e.g. Mylar™), and unplasticized polypropylene. If moisture permeation through the polymer is a concern, aluminum foil laminated between unplasticized polyester may be used. Non-shedding low-extractable polyethylene wrap is available (e.g. Tycleen™ or Marvelseal™).

13.3.2 Containers, Brushes, etc.

Containers and brushes should contain no extractable materials and should be chemically compatible with the material being used. They should be cleaned as scrupulously as the substrates. Teflon™ and other fluoropolymers are good container materials. Brushes should be used with fluids, but if used dry, the pressure should be light to prevent abrasive transfer.

13.3.3 Chemicals

Fluids can be a major source of contamination in processing.[7] It may be necessary to specify and use high purity/particulate-free

chemicals in order to attain the desired contaminant level in the processing environment. If this is necessary, attention should be paid to the packaging and analysis of the fluids (and gases) used.[8] The particle content of a fluid can be monitored during use.[9]

If impure fluids are allowed to dry on a surface they can leave a non-volatile residue which can consist of organic, biological, and/or inorganic materials. These residues can be difficult to remove. Often residues can be detected by visual "fogging" of what should be a clean glass surface after evaporation of some of the solution. More quantitative residue analysis consists of allowing a volume of the chemical to evaporate and then analyzing the residue which remains (*ASTM Method D1353-78*) or by analyzing the particulate residue from a sprayed droplet .[10]–[12] These techniques can detect contamination to one part per billion in a fluid. Residues can be minimized by rinsing in copious amounts of ultrapure water. **Wet surfaces should not be allowed to dry without thorough rinsing with a low residue solution!!!**

Fluid surfaces can be a source of particulate contamination. If the surface is open to the ambient, particles will settle on the surface and float there. When a surface is withdrawn from the solution, the particles on the fluid surface will be "painted" on the solid surface.[13] If this is a problem, the surface should be vapor dried so that the condensing drying fluid flows the particles from the surface. Fluid containers should be covered when not in use to minimize the deposition of particulates on the surface.

13.3.4 Processing Gases

Gas purity can be specified on purchase. Often gases are further purified in the processing environment. Purification of inert gases and hydrogen and nitrogen can be by reaction of oxygen and water vapor with a surface such as a hot uranium, titanium, or copper bed. Purification of some gases can be attained by diffusion through a hot membrane though this typically has a low gas throughput. Hydrogen can be purified by diffusion through platinum, oxygen through silver, and helium through quartz.

Dry Gases

Dry gases are used for storage containers, as dilutant gases for ballasting mechanical pumps, and for backfilling vacuum systems to bring

them up to ambient pressure. Large volumes of dry gas can be obtained from the vaporization of liquid nitrogen (LN) usually from above the LN2 in a tank (1 liter of LN2 gives 650 liters—stp—of dry gas). Large amounts of air can be dried rather inexpensively by compression and cooling. Compression raises the partial pressure of the water vapor above the saturation vapor pressure causing the excess vapor to condense so that it can be drained away. On expansion, the air is very dry. Small volumes of air can be dried by adsorption but the adsorbers must be regenerated. Dry gas can be distributed throughout a plant through PVC plumbing.

The humidity in a room is generally controlled to a specific level by drying the air, usually refrigeration, and then adding moisture in a controlled manner. This is often done with a nebulizer which sprays small droplets of water into the gas flow. Typically 40–45% relative humidity is a comfortable humidity. A very low humidity increases problems with static electricity while a high humidity is uncomfortable, particularly when wearing non-breathable clothing.

High Pressure Gases

High pressure gases are often used in PVD processing. They may be inert gases used for sputtering or reactive gases used for reactive deposition processes. Typically high pressure gases come in tanks pressurized to 2000 psi or so. The gas from the tank passes through a pressure regulator which lowers the gas pressure to 10–100 psi. Then the gas often passes through a mass flow meter and flow control device. Generally the gas manifolding and flow control system on the low pressure side of the regulator can not withstand the full tank pressure if the regulator fails. To prevent the overpressurization of components, a flow restrictor and a pressure relief valve are placed in the line at the regulator output and shown in Fig. 3-14. If the regulator fails, a pressure pulse in the manifold is prevented by the flow restrictor and the pressure relief valve allows the gas to be vented from the manifold.

High pressure gas tanks, particularly those with regulators should be strapped down so that they don't fall, breakoff the valve, and turn into jet-powered projectiles.

Toxic and Flammable Gases

PVD processing typically does not use toxic gases in processing, however in some cases, PVD processing makes use of PECVD-type processing that can utilize toxic and flammable gases. For example, in the reactive deposition of boride and silicide films, the source of boron may be from diborane (B_2H_6) and the source of silicon may be from silane (SiH_4) both of which are toxic and flammable gases. If these types of gases are used, appropriate measures to distribute the processing gases and to dispose of the unused gases and toxic byproducts must be made. In reactive plasma cleaning and etching, often potentially toxic and corrosive gases are used. For example, if CCl_4 has been pumped in the presence of water vapor, phosgene ($COCl_2$)—a highly toxic chemical warfare agent—can be produced and accumulate in the pump oil. Typically toxic gases are distributed through double-walled tubing and disposed of by pyrolysis (burning) or by dissolving in a disposable fluid.

13.4 BODY COVERINGS

The human body is a major source of particulate contamination from skin sloth (dandruff), hair, and aerosol evaporation from breathing, talking and sneezing. The clothing that is worn in the cleaning area should be commensurate with the cleaning level desired. As a minimum, gloves should be worn during the cleaning operation. This is not only to protect the substrate surface but to prevent the cleaning operation from removing the oils from the skin of the operators. If their skin dries out, soon you will find them using moisturizing creams which is a major source of contamination. The next level of contamination-control clothing is a coat of a fabric that does not breathe and is not a source of particulates. Next ,a hair covering should be used since head dandruff, hair, and hair dressing can be a major source of contamination, particularly since touching the head is a common gesture for many people. Next a mouth covering can be added since aerosols generated when speaking or sneezing is a source of fine particulates in the air. This is particularly important if the operator is working close to the substrate surface.

Higher levels of contamination control clothing require using shoe coverings, hoods, zip-up jump suits, and finally totally enclosed

"space-suits" where the ventilation for the suit is connected outside the clean area. The special clothing used to maintain a clean environment can be disposable or reusable. If reusable, the clothing can be bought and cleaned internally, cleaned by a external contractor, or rented from a supplier who is responsible for the cleaning.[14] Clothing should be cleaned and packaged by the supplier commensurate with the cleaning level desired. The Institute of Environmental Sciences (IES) has developed a number of recommended specifications for use in the cleanroom.[15] For example, see "Recommended Practices for Garments" (IES-RP-CC-003-84-T).

13.4.1 Gloves

It is preferable to handle surfaces using fixtures or tools. However, in many cases, the surfaces must be handled directly and gloves should be used.* Gloves may be of a woven fabric or of a polymer film that is either molded to shape or heat welded from flat sheet. Polymer gloves for general use are often coated with talc powder to make donning the gloves easier. For most cleaning applications, un-powdered gloves must be specified in order to avoid particulate contamination. Glove lengths can vary from wrist-length to elbow-length. Liners and half-finger liners can be worn under the gloves to aid in moisture adsorption and comfort. Fingercots, which are individual sleeves that cover the finger tips, are not as desirable as gloves but are more comfortable.

There are a number of choices for polymer glove material including: latex rubber, nitrile rubber, vinyl, polyethylene, and fluorocarbon materials such as Teflon™, as well as polymer blends such as latex-nitrile-neoprene-natural rubber blends for use with acids. All glove material should not be powered and should have "low-extractables" for the chemicals with which they might come into contact.[5,16,17] Vinyl gloves are comfortable and are often used in handling surfaces. A problem with the vinyl is that when in contact with alcohol, a common "wipe-down" material and drying agent, the alcohol extracts phthalate plasticizers from the

*The amount and type of contamination from fingers can vary widely between people. I once had a technician who could not wear stainless steel watch bands because his perspiration would corrode the stainless steel.

vinyl. These extractables on the glove surface can then contaminate surfaces. Generally it is best not to have vinyl gloves in the cleaning area.

Unplasticized polyethylene gloves are compatible with alcohol and most cleaning chemicals and are good gloves for clean handling. They can be obtained on paper rolls such that they are easily donned without touching the external surface of the glove. An advantage of the polyethylene gloves is that they are rather awkward and uncomfortable and operators will readily discard them when they are not required. Latex rubber gloves are often used in "suiting-up" for the clean room and generally use rubber about 7 mils thick. Latex gloves are cheaper than comparable vinyl gloves but they produce more ionic contamination than do vinyl or nitrile gloves.[17] Latex gloves made from natural rubber have been shown to produce allergic reactions in a number of people when used continuously. Latex gloves and finger cots can be obtained with a filler that makes them dissipate static electricity.

A problem with any glove used all day long is that they transfer contamination from one place to another. When handling clean surfaces an unplasticized polyethylene glove should be put on over the latex glove and then discarded when the handling is over. Fluorocarbon materials, such as Teflon™, are very compatible with most chemicals and Teflon™ gloves are available but are expensive. A disadvantage of all polymer gloves is that the soft polymer can be easily transferred to a clean surface by abrasive transfer. Abrasive transfer is dependent on the materials and the adhesion and friction between the surfaces. Another disadvantage of the polymer gloves is that they are slippery and it may be desirable to use fabric gloves such as nylon when handling large or heavy parts.

De-sized and lint-free Nylon™ or Dacron™ woven fabric gloves are used when friction in handling is desirable or abrasive transfer from softer polymer gloves is a problem. The fabric can have conductive fibers woven into the fabric to dissipate electrostatic charge buildup. Woven fabrics will wick oils from the skin to the glove surface, so polyethylene, or latex gloves, or finger cots, should be used under the fabric gloves. Nylon gloves can also be used when handling substrates and fixtures that are too hot for latex or polyethylene gloves. For very hot surfaces a glove of polyimide material such as Nomex™ from Du Pont can be used.

13.4.2 Coats and Coveralls

Body covering comes with several degrees of contamination-control capabilities.[19] The button-up "lab coats" provide the least contamination control. Zip-up coats are better. Zip-up coveralls ("jump suits") or coveralls with built-in foot coverings (bunny suits) are even better. The collar of the coat can be designed to cover the lower part of the face covering. The cloth used in the clothing was discussed in the previous sections. For super clean environments "spacesuits" that completely enclose the worker and are vented outside the clean area can be used. Generally laundered polyester garments are more free of particulates than are disposable garments.[18]

13.4.3 Head and Face Coverings

Headcaps are elastically sealed and are similar to shower caps. The coverings should cover all of the hair. Hoods with neck covering can be used on top of the head caps with the neck covering inside the collar of the coat. Coverings are available for use with beards but beards should be discouraged in very clean environments. In very clean environments, oily hair treatment should be discouraged since operators will tend to pull at their head covering during the day and the hair treatment can end up on the gloves.

Face covering should cover the nose and mouth. The fabric masks should have "pinch-strips" on the nose area to provide a tight fit. The material should breath but not let liquid droplets through. Nylon, which adsorbs water effectively is often used. Some face coverings include paper filters and activated carbon absorbers. There are special face coverings for men who have beards. Head coverings that completely contain the head and filter the air entering and leaving the covering are used in very clean environments.

13.4.4 Shoe Coverings

Generally it is best for each operator to have a special pair of shoes that they leave in the gowning area. Over these shoes, the shoe coverings or "booties" are worn with the top flaps inside coveralls. After gowning, the operator should walk over "sticky" matting to remove any particulates on the bottom of the shoe covers and through an air shower before entering the cleanroom.

13.4.5 Gowning Area

Entrance to the gowning area should be controlled so that there is no unauthorized entry of personnel. This can be a button-type combination lock. The gowning area can be entered through an "air shower" to remove loose particulates.

The procedures and protocols for using cleanroom-type clothing is important.[20][21] An area near the entrance to the cleanroom should be delineated with a line on the floor. People should not be on the "clean side" of the line until they have donned the complete cleanroom covering. There should be a bench along the line where one can sit to donn their covering. Garment storage, lockers for personal belongings, and bins for used garments is kept on the dirty-side of the line.

The gowning protocol is generally as follows:

- Put on hair covering and hood
- While seated with feet on "dirty side" of the line put on a bootie and put that foot on the clean side of the line. Repeat with the other foot.
- Donn coverall, taking care that the surface does not drag on the floor
- Put on face mask
- Put on safety goggles if used
- Put on gloves

Sleeves and ankles can be taped to prevent air flow (breathing) during movement.

13.4.6 Personal Hygiene

Operators can assist in contamination control before they leave home. Oily hair dressings, mascara, powders, and deodorants should not be used. Skin care should avoid dryness which gives rise to skin flaking. Clothing worn under the body covering should be comfortable and not be "itchy." Silk is particularly good in that it is a comfortable, long-fiber material with good ability to adsorb water and body oils.

13.5 PROCESSING AREAS

Contamination in the processing area can be in the form of particulates, vapors, fluids, or solids. Particulates can be airborne and settle on surfaces, or they may be on surfaces and transferred by contact. Electrostatic charging can be a factor in particulate contamination and often ionizers are used to help charge airborne particles and cause them to be attracted to collector surfaces other than the surfaces being cleaned. Vapors can condense on surfaces causing recontamination. Fluids and solids can be transferred to clean surfaces by contact.

Particulate contamination on the substrate surface is the major source of pinholes in films deposited on smooth surfaces. The cost of reducing the particulate contamination in a processing area can vary from not very much when changing housekeeping practices to extremely high if very low particle counts are required. The amount of particulate contamination that is allowable depends on the cleaning, handling, storage, and deposition environment used. In many cases, a particulate contamination problem can be alleviated by changes in processing, handling and storage rather than by changing the ambient. Air filtration allows the fabrication of "clean rooms,"[21] "clean benches," and clean areas.

In the United States, *GSA Federal Standards 209b ("Clean Room and Work Station Requirements: Controlled Environment)* specifies that the number of particles per cubic foot of volume with a size greater than 0.5 microns and none larger than 5 microns (i.e. "Class"), is the standard for specifying an environment. Air filtration with proper flow patterns can provide a Class 10 or better environment. In the metric system, the number of particles per cubic meter is given and the classification is given as an "M Class" where M is the logarithm to the base 10. Class 1 (≈M 1.5), Class 10 (≈M 2.5), and Class 100 (≈M 3.5) cleanrooms are used for building and assembling devices that are very particulate sensitive such as semiconductor device metallization where dust can cause pinholes which cause "opens" in patterned electrical paths. Class 1000 (≈M 4.5) and Class10,000 (≈M 5.5) rooms are used for less sensitive fabrication such as assembly areas. Class 10,000 clean areas can usually be attained by modification of existing areas and proper techniques. A normal un-filtered room will generally be Class 100,000 (≈M 6.6) or even higher. Just because the cleanliness is rated as a certain class does not mean that a particular work volume is that class. There are many effects that can raise the particle count in the local area.

13.5.1 Mechanical Filtration

Airborne particulate contamination may be effectively controlled by mechanical filtration of air flowing through High-Efficiency-Particulate Air (HEPA™) or Ultra-low-Permeation-Air (ULPA) fiber filters.[22–24] These filters can filter 99.999997 % of all particles larger than 0.5 microns in size. The air velocity through the filter should be about 90–100 ft/in in a "laminar" or non-turbulent flow pattern. HEPA™ filters can be made from a variety of materials and filters should be compatible with the processing environment. For instance, it has been reported that salt particles on some filter materials absorb water and degrade the filter to the point that the filter material generates particulates. Particle filters are often arranged in series. For example, there may be a pre-filter for large particles followed by a HEPA™ filter that is 99.97% or better in filtering particles of 0.3 microns or larger, followed by a HEPA™ filter that is 99.999% efficient for 0.12 micron sized particles. The clean environment must be utilized with care in order to maintain a low particle count.[22]–[25] HEPA™ filters do not filter vapors. To the contrary, they can become a source of vapor contamination if the paper filters become saturated with a vapor such as oil.* Vacuum cleaners using HEPA™ filters are available for use in clean areas and in cleaning the deposition chamber and fixturing.

13.5.2 Electronic and Electrostatic Filters

Electronic precipitators use high voltage ionization to ionize particles which are collected on surfaces in the precipitation cell of the filter. Electrets use a surface with a permanent electrostatic charge to

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*As part of a specification for a cleaning process being transferred from the laboratory to production, it was specified that after cleaning, the glass surface must show a contact angle with water of $<5^{o}$. The process engineer in the cleanroom found that they could not meet the specification and requested that the specification be changed. On investigation, it was found that the exhaust of the mechanical pumps was near the intake of the cleanroom—the filters were saturated with oil. The vapor contamination in the cleanroom was similar to that of a machine shop. The surface was recontaminated before they could make the contact angle measurement. The solution to the cleaning problem required a major overhaul of the cleanroom arrangement.

collect particles. Electret materials are plastics that have been heated and stretched in a DC electric field, giving them a permanent surface charge. Electrets can be used in brushes, filters, or as surfaces such as mats.

13.5.3 Humidity Control

Humidity can be an important environmental variable. If too dry, electrostatic charge buildup can be a problem. If too humid, workers are uncomfortable and sweat—which can lead to contamination problems. The most comfortable humidity is at about 40–45% relative humidity. To obtain this humidity, it may be necessary to dry the air and then introduce humidity in a controlled manner.

13.5.4 Floor and Wall Coverings

Walls and floors should be coated with a low-outgassing material (Table 13-1) which is easily cleaned. In some cases the coating material should be electrically conductive to minimize electrostatic charge buildup.

Floors can have floor mats which have a tacky surface to remove and hold particulates carried on footwear. One supplier uses a polyester polymer that has a natural high-tack surface that can be cleaned. The same material can be used on rollers and the rollers are used to remove particles from surfaces.

13.5.5 Cleanrooms

The term "cleanroom" is **misleading** in that the cleanroom only controls particulate contamination and generally nothing is done to actively remove contaminate vapors from the environment. Cleanrooms filter and control the air flow in a specially designed room with the air flow from the ceiling and out through holes in the floor. Air flow in a cleanroom should be checked and monitored using "foggers" to detect and eliminate regions of stagnant flow which prevent proper operation of the filtration. Cleanrooms are generally kept at a positive pressure with respect to the outside so that all air leakage is outward. The pressure differential should be about 0.15 inches of water and should be continuously monitored and recorded. All equipment and processes that have a potential for creating

contamination should be kept out of the cleanroom.* If this is not possible, the processing volume should be accessible through a wall ("bulkhead mounting") while the rest of the system is kept external to the cleanroom. For example, a vacuum system using an oil diffusion pump, should be designed such that the vacuum chamber is accessible through a wall but the pumping stack, and maintenance thereof, is external to the cleanroom. Typically, the cleanroom relative humidity will be controlled to 40–45% for the comfort of the personnel and to minimize static charge buildup on surfaces.

The Institute of Environmental Sciences (IES) has developed a number of recommended specifications for use in the cleanroom. For example:

- Recommended Practices for Testing Clean Rooms—IES-RP-CC-006-84-T
- Recommended Practices for HEPA™ Filters—IES-RP-CC-001-83-T
- Recommended Practices for Laminar Flow Clean-Air Devices—IES -RP-CC-002-83-T

13.5.6 Soft-Wall Clean Areas

Space within a room can be filtered using down-draft HEPA™ filters with walls of plastic sheeting or strips to contain the air flow. The air flow exits at the bottom of the segregated area. This is a low cost alternative to a cleanroom and can often be incorporated into standard high-ceiling industrial buildings or rooms. The downdraft arrangement has the advantage that particles are swept toward the floor from open work

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*Product yield had become a problem in production. The product yield was changing with a two week cycle and no one could determine why. Early one morning, a process engineer noticed a janitor rolling a floor buffer down the ramp leading to the cleanroom door. When asked what he was doing he replied "They tell me that is a cleanroom but they won't let me in to clean it I have to wait until they go home." The janitor had obtained the combination of the door lock from a worker and every two weeks the janitor went in stripped and rewaxed the floors, polished the benches and chairs, and did what he would normally do when cleaning a room. He said that he was getting ready to start cleaning all the funny looking fixtures that were in the cabinets. The janitor was just trying to do his job. The person that gave him the lock combination was fired.

areas.* In some manufacturing configurations, processing is performed in seperated clean areas and the substrates must be transported between the clean areas (Sec. 12.8.2)

13.5.7 Cleanbenches

Cleanbenches use horizontal laminar flow of filtered air from the back to the front of a hooded table. Care must be taken to ensure that the laminar flow is not disrupted by equipment on the bench which can bring particles into the workarea by turbulent exchange with the non-filtered room air.

13.5.8 Ionizers

Ions of gas molecules are injected into the clean room to attach to particulates so that they will deposit on grounded surfaces and prevent static charge buildup on surfaces. The ionizers are generally high voltage ionizers similar to that used in electronic precipitators. A problem with high voltage ionizers using metal electrodes is that the electrodes arc and produce particluates. This can be avoided by using single crystal silicon emitter tips.[26][27]

13.5.9 Particle Count Measurement

Particle counts in a given volume of air in the clean area are measured by light scattering.[28]–[30] Many commercial particle counters are available. For submicron particles, the size of the airborne particle can be increased by vapor phase condensation before counting.[31] The relative particle count in a processing area can be judged by the number of pinholes that are formed in the deposited film—a increase of pinholes probably indicates an increase in particle count though the particulate contamination can be occurring in the deposition system.

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*In visiting a soft-wall clean area, I found that the technician had his desk, books, coat, and everything in the clean area. When asked why, he said that it was the best place that he had found for his allergies.

13.5.10 Vapor Detection

Condensable contamination in the ambient can be detected by adhesion and wettability tests on clean surfaces, by collection on an IR window followed by IR analysis, or by the change of resistivity of some heated oxides (sensors).[1]

13.5.11 Reactive Gas Control

Reactive gases can be present in the cleaning environment.* Such gases can be associated with processes taking place in the cleaning area.** For example, an etching process can be releasing gases such as chlorine which is detrimental to aluminum surfaces. The cleaning environment should be monitored for such gases if they are detrimental to the processing. There are a number of gas sensor on the market. The latest family of sensors are called "electrocatalytic gas sensors" and they are capable of detecting and differentiating among many gases.[32]

13.5.12 Microenvironments

Cleanrooms are a major expense, both to construct and maintain, so other approaches to particulate reduction should be utilized where possible. One approach is to use containerized processing modules where

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*In the use of a UV/O_3 cleaner, it was found that the stainless steel in the UV chamber was corroding rapidly. The problem was traced to chlorine in the air from the sanitization of the evaporative coolers that were being used to cool the air. The chlorine was detected by bubbling the air through a silver nitrate solution and precipitating white AgCl.

**In several installations, Ti-Au thin film metallization was patterned with an iodine etch. One installation had problems with corrosion of the metallization after patterning but the others did not have the problem. Extensive tests showed that the corrosion was due to iodine in the film which when combined with water formed an electrolyte that allowed galvanic corrosion to occur. The main difference in the installations was the ventilation in the etching area. Improved ventilation and the use of a Ti-Pd-Au metallization cured the problem.

the parts are contained and/or processed in small volumes ("microenvironments") which can be joined to form a processing sequence.[33] An example of such a system is the completely contained processing for metallizing and assembling quartz crystal oscillators where vapor and particulate contamination is eliminated to prevent frequency shift due to contamination on the crystal surface during use.[34]

13.5.13 Personnel Training

All personnel working in a clean area should be instructed as to why things are the way they are and the importance of cleanliness. All personnel working in a cleanroom should be trained in the proper procedures for the cleanroom. One person should be designated as the cleanroom monitor. This person should observe cleanroom procedures, instruct or remind individuals as necessary, and prepare a review to be discussed at weekly or monthly review meetings. This person should behave in a non-antagonistic manner (not be a policeman) but rather should promote group awareness and concern. It may be desirable to rotate this responsibility among cleanroom workers.

13.6 SUMMARY

The condition of the ambient external to the deposition environment has a major impact on how much contamination is introduced into the deposition chamber. It is important that this environment be controlled to the necessary level. This includes handling and storage of all the supplies used in the external cleaning and preparation processes as well as the cleaned substrate surfaces.

FURTHER READING

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Surface Contamination, Vol. 1&2, (K. L. Mittal, ed.), Plenum Press (1979)

Handbook of Contamination Control, (D. L. Tolliver, ed.), Noyes Publications (1988)

Contamination Control Handbook, NASA N70-13566 (1969) (available from NTIS)

The OHMI Papers: Challenges to Ultimate Cleanliness in Semiconductor Processing, (R. W. Keeley and T. H., Cheyney, eds.), available from *Micro Magazine*

Compendium of Standards, Practices, Methods, Etc., Relating to Contamination Control, IES-C-CC-009-84-T, available from The Institute of Environmental Sciences

Sax, N. I., *Dangerous Properties of Industrial Materials*, Van Nostrand-Reinhold (1988)

Furr, A. K., *CRC Handbook of Laboratory Safety*, 3rd edition (1989)

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Appendix 1: Reference Material

Some publications and professional societies that may be of interest to the reader include:

A1.1 TECHNICAL JOURNALS AND ABBREVIATIONS

Applied Optics (Optical Society of America)—Appl. Optics

Applied Physics Letters—Appl. Phys. Lett.,

Applied Surface Science—Appl. Surf. Sci.

CRC Critical Reviews—Solid State and Materials Science—Crit. Rev. Solid State, Materials Sci.

IBM Journal Research and Development—IBM J. Res. Dev.

IEEE Circuits and Devices—IEEE Circuits Devices

International Journal of Nondestructive Testing—Internat. J. Nondestructive Test.

Japanese Journal of Applied Physics—Jpn. J. Appl. Phys.,

Journal of Adhesion—J. Adhesion

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Journal of Adhesion Science and Technology—J. Adhesion Sci. Technol.

Journal of American Ceramic Society—J. Am. Ceram. Soc.

Journal of the American Chemical Society—J. Am. Chem. Soc.

Journal of Applied Physics—J. Appl. Phys.,

Journal of Coating Technology—J. Coat. Technol.

Journal of the Electrochemical Society—J. Electrochem. Soc.

Journal of Material Science—J. Mat. Sci.

Journal of Materials Research—J. Mat. Res.

Journal of Nuclear Materials—J. Nucl. Mater.

Journal of Vacuum Science and Technology—In 1983 the Journal was divided into two sections

Section A (Vacuum, Surfaces and Films)—J. Vac. Sci. Technol. A

Section B (Microelectronics and Nanometer Structures)—J. Vac. Sci. Technol. B

Materials Research Society Bulletin—MRS Bulletin

Metal Finishing—Metal Finishing

Metallography—Metallography

Nuclear Instruments and Methods in Physics Research—Nucl. Instrum. Method. Phys. Res.

Physical Review—Phys. Rev.

Plasma Chemistry and Plasma Processing—Plas. Chem. Plas. Proc.

Plating and Surface Finishing (formally Plating)—Plat. Surf. Finsh.

Radiation Effects—Rad. Effects

RCA Review—RCA Review

Review of Scientific Instruments—Rev. Sci. Instrum.

Scanning—Scanning

Surface and Coating Technology—Surf. Coat. Technol.,

Surface Science—Surf. Sci.

Surface and Interface Analysis—Surf. Interface. Analysis.

Thin Solid Films—Thin Solid Films

Training and Development—Train. Dev.

Vacuum—Vacuum

Vacuum Techniques: Applications & Ion Physics (England)—Vac. Tech.

Wear—Wear

A1.2 PERIODICALS AND ABBREVIATIONS

(Complementary subscriptions to qualified persons)

Cleanrooms (PennWell Publishing Co. 603/891-0123)—*Cleanroom.*

Cleanroom Technology (Angel Business Communications, Kingsland House, 361 City Road, London EC1V 1LR, England)—*Cleanroom Technol.*

Converting Magazine (Cahners Publishing Co., 847/390-2405)—*Convert. Mag.*

Micro (formally Microcontamination) *Magazine* (Canon Communications, 310/392-5509)—*Micro* or *Microcontamination*

Physics Today [American Institute of Physics (AIP), 516/576-2200]—*Physics Today*

Precision Cleaning (Witter Publishing Co., 908/788-0343)—*Precision Clean.*

Product Finishing (Gardner Publications, 513/231-8800)—*Prod. Finish.*

R&D Magazine (Cahners Publishing Co., 847/635-8800)—*R&D Mag.*

Semiconductor International (Cahners Publishing Co., 847/635-8800)—*Semicond. Internat.*

Solid State Technology (PennWell Publishing Co., 603/891-0123)—*Solid State Technol.*

Superconductor Industry (Rodman Publishing Corp., 201/825-2552)—*Supercond. Ind.*

A1.3 OTHER

Advanced Coating & Surface Technology—Monthly news bulletin from Technical Insights, Inc., industry news, patents, meetings, etc. (201/568-8247)

Surface Modification Technology News—Monthly news bulletin (subscription) from Business Communications Co. (203/853-4266)

Thin Film/Diamond Technology News—Monthly news bulletin (subscription) from Business Communications Co. (203/853-4266)

Proceedings of the Annual Technical Conferences, Society of Vacuum Coaters, SVC Publications—Prior to 1981, ISSN 0731-1699. Subsequent to 1981, ISSN 0737-5921 (505/856-7188)

SVC Educational Guides, SVC Publications—60 plus one page descriptions of various aspects of PVD processing and materials science (505/856-7188)

A1.4 BUYERS GUIDES, AND PRODUCT AND SERVICES DIRECTORIES

Buyers Guides assist in finding sources for materials and equipment needed for the various processes discussed in this book. Publishers of Buyers Guides include:

Association of Vacuum Equipment Manufacturers (AVEM)—Products and services for the vacuum industry

Converting Magazine—Web handling equipment

Laser Focus World—Electro-optic equipment & supplies

Metal Finishing Magazine (Metal Finishing Guidebook and Directory)—General industrial finishing equipment and supplies

Micro (previously *Microcontamination*)—Cleanroom supplies

Physics Today—General laboratory equipment and supplies

Products Finishing—General industrial finishing equipment and supplies

Research and Development Magazine—General laboratory equipment and supplies

Solid State Technology Magazine—Equipment and supplies associated with the semiconductor industry

Semiconductor International—Equipment and supplies related to the semiconductor industry

Superconductor Industry Magazine—Equipment and supplies related to the superconductor industry

Thomas Register—General commercial products & services

Society of Vacuum Coaters: Product and Services Directory—Contract thin film deposition companies, new & used vacuum equipment suppliers, consultants to the PVD industry

A1.5 SOCIETIES, ASSOCIATIONS, AND OTHER ORGANIZATIONS

There are a number of technical societies, organizations, and trade associations who have interests relevant to this book. They include:

The Adhesion Society
Room 2
Davidson Hall
Virginia Tech
Blacksburg, VA 24061-0201
540/231-7257

American Chemical Society (ACS)
1155 16th St. NW
Washington, DC 20036
202/872-4600
Fax: 202/872-4615
web site: www.acs.org

American Electroplaters and Surface Finishers Society (AESF)
12644 Research Parkway
Orlando, FL 32826-3298
407/281-6441
Fax: 407/281-6446
web site: www.aesf.org

American National Standards Institute (ANSI)
11 West 42nd Street, 13th Floor
New York, NY 10036
212/642-4900
Fax: 212/398-0023
web site: www.ansi.org

American Institute of Physics (AIP)
500 Sunnyside Boulevard
Woodbury, NY 11797
800/874-6383
Fax: 516/349-9704
web site: www.aip.org

ASM International (ASM)
(formerly American Society for Metals—until 1987)
9639 Kinsman Road
Materials Park, OH 44073-0002
440/338-5151
Fax: 440/338-4634
web site: www.asm-intl.org

American Society for Nondestructive Testing (ASNT)
1711 Arlington Lane, P.O. Box 28518
Columbus, OH 43228-0518
614/274-6003
Fax: 614/274-6899
web site: www.asnt.org

American Society for Testing Materials (ASTM)
100 Barr Harbor Dr.
West Conshohocken, PA 19428
610/832-9500
Fax: 610/832-9555
web site: www.astm.org

American Society of Metallurgical Engineering (ASME)
345 East 47th Street
New York, NY 10017-2392
212/705-7722
Fax: 212/705-7739
web site: www.asme.org

American Vacuum Society (AVS)
120 Wall St., 32nd Floor
New York, NY 10005
212/248-0200
Fax: 212/248-0245
web site: www.vacuum.org

Association of Vacuum Equipment Manufacturers (AVEM)
440 Live Oak Loop
Albuquerque, NM 87122
505/856-6924
Fax: 505/856-6716
web site: www.avem.org

Chemical Coaters Association International (CCAI)
P.P. Box 54316
Cincinatti, OH 45254
513/624-6767
Fax: 513/624-0601
web site: www.finishing.com

Electrochemical Society (ECS)
10 S. Main St.
Pennington, NJ 08534
609/737-1902
Fax: 609/737-2743
web site: www.electrochem.org

Institute of Electrical and Electronic Engineers (IEEE)
445 Hoes Lane
Piscataway, NJ 08855-1131
800/678-4333
Fax: 732/981-9667
web site: www.ieee.org

Institute of Environmental Sciences (IES)
940 E Northwest Hwy
Mt. Prospect, Il 60056
847/255-1561
Fax: 847/255-1699
web site: www.insten.vsci.org

Institute of Metal Finishing (IMF)
Exeter House, 48 Holloway Head
Birrmingham, B1 1NQ
United Kingdom
44/1216227387
web site: www.uk-finishing.org.uk

International Society for Hybrid Microelectronics (ISHM)
1850 Centennial Park Dr. Suite 105
Reston, VA 22090-2698
703/471-0066
Fax: 703/758-1066
web site: www.ishm.ee.vt.edu

International Society for Optical Engineering (SPIE)
1000 20th Street
Bellingham, WA 98225
206/676-3290
Fax: 206/647-1445
web site: www.spie.org

International Standards Organization (ISO)
Technical Committee #107 - Metallic & Other Inorganic Coatings
1 rue de Varembe, Case postale 56, CH-1211 Geneve 20
Switzerland
41/227490111
Fax: 41/2273333430
or through ASTM Committee E42.94—the Technical Advisory Group to ISO

Materials Research Society (MRS)
506 Keystone Dr.
Warrendale, PA 15086-7573
412/779-3003
Fax: 412/779-8313
web site: www.mrs.org

Metal Finishing Supplier's Association (MFSA)
801 N. Cass Ave.
Westmont, IL 60559
630/887-0797
Fax: 630/887-0799

National Association of Corrosion Engineers (NACE)
1440 S. Creek Dr.
Houston, TX 77084-4906
281/228-6200
Fax: 281/228-6300
web site: www.nace.org

National Association of Metal Finishers (NAMF)
209 Elden Street, Suite 202
Herndon, VA 20170
703/709-8299
Fax: 703/709-1036
web site: www.nmfrc.org (host web site)

Optical Society of America (OSA)
2010 Massachusetts Ave.
Washington, DC 20036
202/223-8130
Fax: 202/223-1096
web site: www.osa.org

Semiconductor Equipment and Materials International (SEMI)
805 East Middlefield Road
Mountain View, CA 94043-4080
415/964-5111
Fax: 415/967-5375
web site: www.semi.org

SEMATECH
2706 Montopolis Dr.
Austin, TX 78741-6499
512/356-3081
FAX: 512/356-7118
web site: www.sematech.org

Society for the Advancement of Materials and Processing Engineering (SAMPE)
1611 Parkins Dr.
Covina, CA 91724
818/331-0616
Fax: 626/332-8929
web site: www.et.byu.edu/~sampe

Society of Automotive Engineers (SAE)
(SAE Publications)
400 Commonwealth Dr.
Warrendale, PA 15096
412/776-4841
Fax: 412/776-5760
web site: www.sae.org

Society of Manufacturing Engineers (SME)
One SME Drive
P.O. Box 930
Dearborn, MI 48121
313/271-1500
Fax: 313/271-2861
web site: www.sme.org

Society of Vacuum Coaters (SVC)
440 Live Oak Loop
Albuquerque, NM 87122
505/856-7188
Fax: 505/856-6716
web site: www.svc.org

The Minerals, Metals and Materials Society (TMS)
420 Commonwealth Drive
Warrendale, PA 15086
412/776-9000
Fax: 412/776-3770
web site: www.tms.org

A1.6 PUBLISHERS

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ASM Publications
9639 Kinsman Road
Materials Park, OH 44073-0002
Tele: 440/338-5151
Fax: 440/338-4634

AVS Publications
120 Wall St., 32nd Floor
New York, NY 10005
Tele: 212/248-0200
Fax: 212/248-0245

Elsevier Science
P.O. Box 945
New York, NY 10159-0945
Tele: 212/633-3730
Fax: 212/633-3680

Cahners Publishing Co.,
Tele: 847/635-8800

Canon Communications,
Tele: 310/392-5509

Gardner Publications,
Tele: 513/231-8800

Institute of Physics Publishing
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New York, NY 10158
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Monticello, NY 12701
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369 Fairview Ave.
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Elsevier Press
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Fax: 212/633-3680

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Tele: 505/856-7188
e-mail info@svc.org

Witter Publishing Co.,
Tele: 908/788-0343

A1.7 WEB SITE INDEX

American Chemical Society	www.acs.org
American Electroplaters and Surface Finishers Society	www.aesf.org
American Institute of Physics (AIP)	www.aip.org
American National Standards Institute	www.ansi.org
American Physical Society	www.aps.org
American Society for Nondestructive Testing (ASNT)	www.asnt.org

American Society for Testing Materials (ASTM)	www.astm.org
American Vacuum Society (AVS)	www.vacuum.org
ASM International	www.asm-intl.org
Association of Vacuum Equipment Manufacturers	www.avem.org
Center for Defense Information	www.cdi.org
Chemical Coaters Association International (CCAI)	www.finishing.com
Defense Technical Information Center (DTIC)	www.dtic.dla.mil
Electrochemical Society	www.electrochem.org
Elsevier Science	www.elsevier.com
Surface and Coating Technol—contents on-line	
Thin Solid Films—contents on-line	
Vacuum—contents on-line	
Finishing Industry (misc)	www.finishing.com
Institute of Metal Finishing (UK)	www.uk-finishing.org.uk
International Society for Hybrid Microelectronics (ISHM)	www.ishm.ee.vt.edu
Institute of Electrical and Electronic Engineers (IEEE)	www.ieee.org
Institute of Environmental Sciences (IES)	www.insten.vsci.org
Institute of Physics Publishing	www.iop.org
International Society for Optical Engineers (SPIE)	www.spie.org
John Wiley (publisher)	www.wiley.com
Material Research Society (MRS)	www.mrs.org
The Minerals, Metals and Materials Society (TMS)	www.tms.org
National Association of Corrosion Engineers (NACE)	www.nace.org
National Association of Metal Finishers (NAMF)	www.nmfrc.org (host web site)
National Institute of Standards and Technology	www.nist.gov
National Metal Finishers Resource Center (NMFRC)	www.nmfrc.org
National Technical Information Service	www.ntis.gov
Optical Society of America	www.osa.org
Photonics Resource Center	www.optics.org
R&D Magazine	www.rdmag.com
Society for the Advancement of Materials and Processing Engineering (SAMPE)	www.et.byu.edu/~sampe
Society of Automotive Engineers (SAE)	www.sae.org

Society of Manufacturing Engineers (SME)	www.sme.org
Society of Vacuum Coaters	www.svc.org
Semiconductor Equipment and Materials International	www.semi.org
Semiconductor International	www.semiconductor-intl.com
Solid State Technology	www.solid-state.com
Thomas Register	www.thomasregister.com

Appendix 2: Transfer of Technology from R&D to Manufacturing

An important aspect of any manufacturing business is to move a product or process from the conceptual stage into manufacturing ("technology transfer"). The goal is to have a "quality" product or process. Quality may be defined in many ways: for instance, 'The ability to meet or exceed the customer's (internal or external) expectations,' (although this may have more to do with "value" than quality), or the 'Ability to meet standards' or 'High reliability' or 'Low maintenance.'

In manufacturing, one major aspect of quality is 'Lack of variability,' i.e. reproducibility. Quality in production means having reproducible processing equipment and materials; comprehensive Specifications, Manufacturing Processing Instructions (MPIs) and "Travelers;" operators trained to follow the instructions; and product testing which reveals variability in a short time frame after production. These factors are considered in a "quality audit" of the manufacturing process.[1] "Manufacturability" means (or should mean) the ability to make a quality product at a profit. In R&D, "quality" is more subjective but includes the ability of others to reproduce the work—his means reproducible experimental conditions, calibrated instruments and controls, and accurate recording of experimental results.

A2.1 Stages of Technology Transfer

The stages involved in taking a process from the laboratory into manufacturing may be defined as:

- Research and development (R&D)
- Process development
- Manufacturing development
- Early manufacturing
- Mature manufacturing

These stages generally overlap one another.

A2.2 Organization

In many organizations, particularly large ones, responsibilities are broadly divided into R&D and Manufacturing which are often separated physically as well as organizationally. These broad areas may be subdivided into groups with specific responsibilities such as:

- Management/supervision—in a group or over a group
- R&D group
- Analytical support group
- Manufacturing development
- Manufacturing
- Quality control
- Other specialties—sales, patent department, design, training, Environmental Safety and Health (ES&H), outside consultants, etc.

Management

In addition to the business decisions on the need for a process, upper and middle Management has the responsibility for determining the "manufacturing feasibility" of the process, establishing goals, milestones and time-tables, allocating the budget necessary to accomplish the goals, and in **organizing and facilitating communications** between groups. The latter role is one of the most important in transferring technology from

R&D to Manufacturing. All levels of Management have the responsibility for implementing the actions needed to reach the goals.

R&D Group

R&D has the responsibility to determine the "best" process ("enabling technology") using materials, equipment and processes that can be "scaled-up" to production levels and yields. R&D begins the process of process development by defining the important process parameters and establishing the process parameter "windows" (limits) which will result in the desired properties of the processed materials. R&D should strive to develop processes with the widest possible process windows (i.e. a "robust" process). Data about the processing and product is provided to Management for their determination of "manufacturing feasibility." The R&D group initiates the writing of "specifications" which are one of the formal means of communication between R&D and the Manufacturing organization. R&D is responsible for conducting a literature (including patent) search on the subject, if appropriate. As process development progresses, R&D supports the Manufacturing Development organization.

Analytical Support Group

The Analytical Group provides support to other groups. In general it is not their sole responsibility to interpret the data they generate. They work with the scientist and engineers to determine what the data means. This may mean developing special controlled experiments to provide data and understanding of a problem or observation. The Analytical Group, along with R&D and QC, is involved in failure analysis of a product that has been placed in-service. This failure analysis can provide questions to be addressed by R&D or feedback from which processing can be improved.

Manufacturing Development

Manufacturing Development is a part of Manufacturing which develops specific processing, monitoring and control equipment and techniques, develops specifications with the assistance of R&D, develops "Manufacturing Processing Instructions" (MPIs), "Travelers," and "Equipment Logs" for use in manufacturing. Manufacturing Development also automates the

processing as much as is desirable. In addition, Manufacturing Development develops "quality" suppliers (along with QC) and supports Manufacturing. "Process Engineers" from Manufacturing Development should begin interacting with R&D early in the process development activity and convey the needs and concerns of Manufacturing to the persons in R&D and to Management. The activities in Manufacturing Development should be formally reviewed periodically with R&D and Management in "process review" meetings. These meetings can result in new questions for R&D to address.

Manufacturing

In Manufacturing "knob-twiddling" is minimized, automation, monitoring and control are further developed, and efforts are made to increase yields and reduce unit costs. In "Early Manufacturing" some degree of change is occurring. In "Mature Manufacturing" changes are minimal.

Quality Control

The Quality Control (QC) organization helps develop characterization techniques, statistical process control methodologies and develops data for yield and reliability prediction.[1][2] QC works with Manufacturing Development to develop reliable and "qualified" suppliers of materials and components from outside sources, and "acceptance tests" for in-coming material. QC is often responsible for failure analysis of product returned from service.

Other Specialties

Other persons and groups may have an input into the transfer process and the time-scale associated with the transfer. For example, the Environmental Safety and Heath (ES&H) organization can have the final say as to what chemicals can be used in the workplace. The use of outside consultants depends on the amount of non-involved in-house expertise available. If such in-house expertise is not available, outside consultants can be used profitably to evaluate the initial concept, the approach to process development, aid in process review, advise on major purchases, and participate in problem-solving. The Consultant can provide specific information and can also provide a perspective different from that developed from the in-house efforts.

Figure A2-1 shows an example of the generalized involvement of each group in the flow from concept through manufacturing.[3] Note the overlapping of involvement.*

A2.3 R&D and Manufacturing "Environments"

The "environments" of R&D and Manufacturing are quite different. In the R&D environment, the personnel are well trained, "creativity" is encouraged, and "knob-twiddlers" are common. Personnel are motivated to write and present papers, to keep current on the pertinent literature and to interact with their peers outside of the company. "Success" is judged rather subjectively by Management. Management is often closely involved in the work leading to an interactive management style.

In the manufacturing environment, personnel are expected to follow directions so that reproducible processing is attained. This tends to stifle "creativity" and often leads to authoritarian management/supervision styles. Automation tends to dissociate the operator from the product, again this stifles "creativity." "Success" in manufacturing is judged by product "out-the-door" and this can lead to friction between groups and "shifts" when "non-productive" activities such as cleaning, maintenance, and calibration are put-off by one group so another has to do the "non-productive" work. Often, seniority rather than knowledge or ability gives manufacturing personnel the "best" jobs. Manufacturing is often a very stressful environment as personnel strive to meet "production quotas."

These differing "environments" lead to differing "cultures" in the two groups. In the extreme, the manufacturing people view the R&D people as elitist and the R&D people view the manufacturing people as drones. Recognition of the differences in environment, basis for performance evaluation, and "cultures" is essential to establishing good communication and a harmonious working relationship between the groups. In order to facilitate communication, the responsibilities of each group and their importance to the company need to be defined and understood by each group.

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*A product had been developed in an R&D organization using rather elaborate cleaning processes and special cleaning agents. When the process was to be transferred to production, they were told that soap and water, and not a lot of that, could be used for cleaning. This meant that the process specifications had to be redefined and extensively rewritten.

Figure A2-1. Transfer of technology from R&D to Manufacturing—relative involvement of the groups.

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A2.4 Communication

In order to effectively transfer a technology from the laboratory to manufacturing, it is necessary to establish both formal and informal communication from the R&D scientist and engineer to the production engineer to the hourly-paid production operator. This communication is often made difficult by the environment that is created in each group by the differing cultural, language, educational backgrounds, responsibilities, goals, basis for performance evaluation, peer interactions on the job and outside of work, and personalities of the persons involved.

Formal communication methods include written Specifications and Manufacturing Processing Instructions (MPIs). Meetings provide another formal means of communication. To be successful, the meetings must be organized so as to have a defined purpose(s). The meeting effectiveness can be enhanced by having a "facilitator" to control and lead the discussion. Generally, the facilitator should be "neutral" and not someone of authority that will stifle discussion and interaction. Persons conducting meeting and persons involved in the meetings, should understand the mechanics and dynamics of a successful meeting.[4]

Informal communication between disparate groups or people can be encouraged by having them work together for a common goal, such as writing a specification or performing a definitive experiment, which is evaluated by someone having the potential to impact their performance evaluation.

A2.5 Styles of Thinking

In order to have effective communication between individuals, it is necessary to understand how individuals think and to recognize that persons who do not think with the same style often have difficulty communicating with each other. The styles of thinking may be divided as follows:[5]

- *Synthesist*—sees likeness in apparent un-likes; seeks conflict; interested in change.
- *Idealist*—welcomes broad range of views; seeks ideal solutions.
- *Pragmatist*—whatever works; seeks shortest route to payoff

- *Analyst*—seeks "one best way;" interested in scientific solutions; often judgmental
- *Realist*—relies on "facts" and expert opinions; interested in concrete results

Personal styles of thinking may be strongly one type or another or they may be combinations of types. The type(s) of thinking style(s) can be determined by testing. If a strong synthesist and a strong analyst are asked to communicate, there can be problems since they "don't think alike." Management needs to recognize these differences and organize the communication methods to overcome these differences. Individuals should be cognizant of their thinking style and recognize that others may have different styles of thinking.

A2.6 Training

A major factor in quality manufacturing is the production technician and operator. An important aspect of manufacturing is "formal training" in classes and "on-floor training" of the manufacturing personnel. On-floor training by peers should be carefully monitored to prevent "bad habits" from developing and being passed-on. Training methods can be categorized as the "Behaviorist" approach and the "Humanist" approach. The behaviorist approach stresses specific knowledge and is amenable to testing on specifics. This type of training is particularly applicable to training operators for repetitious jobs. The humanist approach stresses the reasons and "why" of things. This knowledge is more difficult to test but can lead to more creativity from the individual. The type of training that is effective will vary for each individual.[6]

In training personnel, it should be realized that different people have different learning modes. On one extreme there is the person who primarily learns by seeing ("visual learner") and on the other extreme there is the person who learns primarily by hearing ("auditory learner"). This means that training must be flexible and should contain both visual and auditory material in order to reach the greatest number of people effectively. Also, learning, for many people, can be facilitated by "chunking" the information into small units that can be assimilated easily and by relating the information to something that they already know. Learning should be reinforced by "doing" in a controlled environment to prevent "bad habits" from being developed.

Persons in Manufacturing may be creative but have their creativity stifled by the need to have reproducible processing. The lack of involvement in the process, particularly when the process is highly automated, can affect moral and their sense of accomplishment. Efforts should be made to keep the operator involved in the processing and the results of the processing. For example, publication of daily product throughput and yield data helps keep the operators informed. If the process is automated to such an extent that inattention is a problem, efforts should be made to force involvement. For example, the Travelers should be designed to force operator involvement (e.g. read a meter) even though the information obtained may be redundant. Creativity can be promoted by having mechanisms that allow ideas to be recognized and evaluated without uncontrolled deviation from the MPIs. Such things as "suggestions boxes" and "quality circles" may be used to express ideas which can then be evaluated before being incorporated into the Specifications and MPIs. Individuals, groups, and "shifts" should be made accountable for the product that they produce and a spirit of friendly competition should be encouraged.

In evaluating personnel for being trained as operators for PVD equipment, some of the things that should be evaluated are: written and verbal comprehension, written and verbal communication, and manual dexterity. These can be tested with the appropriate tests.

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4. Doyle, M., and Straus, D., *How to Make Meetings Work*, Jove Publications (1982)
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6. Newstrom, J. W., and Lengnick-Hall, M. L., *Train. Dev.*, 45(6):43 (1991)

Glossary of Terms and Acronyms used in Surface Engineering

Abnormal glow discharge (plasma)–The DC glow discharge where the cathode spot covers the whole cathode and an increase in the voltage increases the cathode current density. This is the type of glow discharge used in most plasma processing. See *Normal glow discharge.*

Abrasion test (characterization)–Testing a film adhesion and abrasion resistance by rubbing, impacting or sliding in contact with another surface or surfaces. Examples: tumble test, tabor test, eraser test.

Abrasive (cleaning)–A material, such as a particle or a rough solid, that is capable of removing material from a surface when there is pressure and movement between the material and the surface.

Abrasive cleaning–The removal of surface material (gross cleaning), including contamination, by an abrasive action.

Abrasive compound–A material used to remove material from a surface by abrasion. Surface smoothness after abrasion is a secondary consideration. Examples: silicon carbide, emery, silica, alumina. See *Polishing compound.*

Abrasive flow machining (vacuum technology)–A means of smoothing a surface using a slurry of abrasive particles in a fluid that is passed over the surface. Also called *slurry polishing.*

Abrasive transfer, contamination by (cleaning)–Transfer of material to a clean surface by contact or friction with a material to which it adheres such as a polymer on a high surface energy surface or chromium on a clean oxide surface.

Abrupt-type interface (film formation)–The interface that is formed between two materials (A and B) when there is no diffusion or chemical compound formation in the interfacial region. The transition of A to B in the length of a lattice parameter (≈3Å). See *Interface.*

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Absolute humidity–The amount of water vapor in the air as measured in grams per cubic centimeter.

Absorbate–The material being absorbed.

Absorption–Condition where the material on the surface (absorbate) diffuses into the bulk of the material (absorbent). See *Adsorption.*

Absorptivity (optics)–The absorption of radiation as it passes through a material. See *Coefficient of extinction*.

Accelerated life test (stress test, adhesion)–A test conducted at a stress higher than that encountered in normal operation for the purpose of producing a measurable effect such as the loss of adhesion, in a shorter time than experienced at normal operating conditions. Example: elevated temperatures, concentrated chemical environment.

Acetylene (C_2H_2) (reactive deposition)–A hydrocarbon gas that is used as a chemical vapor precursor to provide carbon in reactive deposition processes.

Acceleration due to gravity (g)–Acceleration equal to the standard acceleration due to gravity or 9.80665 meters per second per second.

Acceptor–An impurity (dopant) that decreases the number of free electrons in the material. See *Donor*.

Accuracy–The closeness of agreement between an observed value and an accepted reference value. See *Precision*.

Acetone (cleaning)–Solvent with the chemical formula CH_3COCH_3, also known as *2-propanone*.

Acid–Any chemical species capable of supplying a proton (hydrogen ion) to react with another chemical species. An acid yield hydrogen ions (H^+) by reaction with the solvent while a base forms hydroxyl ions, OH^-. See *Lewis acid*.

Acid pickling (cleaning)–Removal of the heavy oxide layer, such as a mill-scale, on a metal by acid etching.

Acidic surface (adhesion, film formation)–A surface capable of accepting an electron from an atom in contact with it.

Acoustic–Relating to sound which is the transmission of a property, such as pressure, through a medium. Sound in the auditory range of the human ear (30 Hz to 16 kHz) is called sonic, above the auditory range (>16 Hz) it is called ultrasonic; and below the auditory range (<30 Hz), infrasonic.

Acoustic emission (adhesion)–The acoustic (sound) emission from a material being fractured or in some cases deformed.

Acoustic streaming (cleaning)–The currents in the fluid that are setup by the acoustic transmission through the fluid in ultrasonic cleaning. Capable of carrying particulates from the bottom of the tank into the cleaning area.

Actinometry (plasma technology)–Compares the emission interactions of the excited states of reference and subject species to obtain the relative concentrations of the ground states of the species.

Activated carbon–A form of carbon that has a very high surface area (>1000 M^2/g) due to the large number of fine pores in the material. Can be regenerated (lose adsorbed gases) at room temperature.

Activated Reactive Evaporation (ARE) (PVD technology)–Evaporation through a plasma of reactive gas in order to deposit a film of a compound material. The plasma activation increases the reaction probability and decreases the pressure of reactive gas needed to form the compound material.

Activation, plasma–The process of making a species more chemically reactive by excitation, ionization, fragmentation or forming new materials in a plasma.

Activation energy–The energy barrier that isolates one chemical state from another as viewed from the reactant side.

Active film–A film that will change properties (color, electron emission, optical transparency) under an externally applied stimulus (electric field, temperature, mechanical deformation). See *Passive film*.

Active gas–A gas that will chemically react with an atom or molecule. Also called a *reactive gas*. See *Inert gas*.

Active storage (cleaning)–Storage in an environment that is continually being cleaned to remove potential contaminants. See *Passive storage*.

Adatom (film formation)–The atom that has been deposited on the surface and that is still mobile (not condensed) on the surface.

Adatom mobility (film formation)–The degree to which an adatom can move on the surface and condense at a nucleation site. The lower the mobility, the higher the nucleation density. See *Nucleation density*.

Addition agents (electroplating)–Chemical agents added to the electroplating bath in order to influence some property of the deposited coating. Example: brightening agents, complexing agents, leveling agents, grain refiners. Also called *additives*.

Adhesion–The physical bonding between the two surfaces of different materials. See *Cohesion*.

Adhesion, apparent–The adhesion observed by applying an external force. If the internal stress is high the apparent adhesion may be low even though there is strong bonding at the interface because the internal stress adds to the applied external stress to cause failure. Also called *practical adhesion*.

Adhesion failure–Failure in the interfacial region (or near the interfacial region) by fracture or deformation. Also called *de-adhesion*.

Adhesion test–A test to give an indication of the adhesion and to ensure product reproducibility. Often the adhesion test is used in a comparative manner to compare to previous findings.

Adhesion test, bend–A comparative adhesion test in which the coated substrate is bent around a rod with a specified diameter. The deformed coating is observed visually and subjected to a tape test.

Adhesion test, breath–An adhesion test that uses the internal stress in the film and the condensation of water from a persons' breath, which enhances fracture propagation in a brittle material, to cause visual adhesion failure. Also called the *Mattox Bad Breath Adhesion Test.*

Adhesion test, indentation–A comparative adhesion test where the surface is indented with a tip of a specific configuration and the fracture of the film around the indentation is observed visually.

Adhesion test, non-destructive–A test that can be performed to establish the presence of a specified amount of adhesion without destroying the film. Example: tape-test of a mirror surface, pull-to-limit wire-bond test.

Adhesion test, scratch test–An adhesion test whereby a loaded stylus with a specific tip configuration is pulled across the film surface under increasing load. The scratched surface is then observed visually for flaking and de-adhesion and is correlated to the load at that point. Acoustic emission during scratching may also be monitored.

Adhesion test, stud-pull test–An adhesion test whereby a protrusion (stud) is bonded to the surface of the film and pulled in tension.

Adhesion test, tape test–A comparative go or no-go (pass or fail) adhesion test where an adhesive tape is applied to the surface of the film and pulled. If the film remains on the surface the adhesion is deemed good. May be used as a non-destructive adhesion test. The tape can be examined for pull-outs. See *Non-destructive test*.

Adhesion test, topple test–Where a bump is bonded to the film surface and pushed from the side until failure.

Adhesion test, wire-pull test–An adhesion test where a wire is bonded to the film surface, often by thermocompression bonding, and then pulled until the wire breaks or the bond fails. The wire-bond test can be used in a non-destructive manner by pulling to a given pull then using the wire in subsequent processing if the bond does not fail.

Adhesion test program–A program designed to subject the film-substrate structure to the stresses (mechanical, chemical, thermal, fatigue) that it might see in subsequent manufacturing, and service with adhesion testing to ensure the adhesion of the film under those conditions.

Adiabatic process–A process where there is no gain or loss of heat to the surroundings.

Adsorbent–The material doing the adsorbing.

Adsorbent capacity–The amount of material the adsorbent can hold before becoming saturated. Example: grams of water per gram of Zeolite™.

Adsorption–Condition where material (adsorbate) is retained on the surface of the bulk (adsorbent). See *Absorption*.

Adsorption pump, vacuum (vacuum technology)–A capture-type vacuum pump that pumps by cryocondensation or cryotrapping on a surface whose temperature is less than -150°C. See *Vacuum pump*.

Aerosols (cleaning)–A suspension of very fine solid or liquid particles in a gas. The evaporation of the liquid aerosol produces very fine particulate contamination from the residue.

Afterglow (plasma)–The region outside the plasma-generation region where long-lived plasma species persist. Also called *downstream location* or *remote location*.

Agglomeration (film growth)–Collecting into isolated regions (clumps).

Agile manufacturing–A modular manufacturing line organized such that the product can be changed easily. Example: From left-hand drive cars to right-hand drive cars.

Aging, natural–The change of property with time under normal conditions. See *Accelerated aging*.

Agitation (cleaning)–The introduction of turbulence into a fluid to enhance mixing and disrupt boundary layers near surfaces.

Air–The ambient gases that are breathed. Air contains gases, vapors and organic and inorganic particles.

Air, medical–Air that has been compressed and contains no substances, such as oil or carbon monoxide, that would be detrimental to a persons health. Also called *SCUBA* (Self Contained Breathing Apparatus) air.

Air fire (cleaning)–Heating of a surface to a high temperature, in an air furnace or an oxidizing flame, to cause oxidation of contaminates. Example: air fired alumina ceramics at 1000°C.

Air knife (cleaning)–A shaped jet of high-velocity air used to blow water from a surface as it passes in front of the air knife. See *Drying*.

Air shower (cleaning)–A downward flow of air used to blow particulates from the surface of clothing after donning cleanroom-type garments.

Alcohol (cleaning)–Any class of organic compounds containing an OH^- group. Often used for wipe-down cleaning and drying.

Alcohol, anhydrous–An alcohol without water. Used as a wipe-down agent and to displace water from a surface.

Alcohol, denatured–Ethyl (grain) alcohol containing a material (denaturant) that makes it unfit to drink. Many materials used to

denature alcohol will leave a residue on evaporation.

Aliphatic solvent (cleaning)–A type of solvent that consists of straight-chain hydrocarbons such as hexane and naphtha.

Alkaline cleaner (cleaning)–A basic cleaner that cleans by saponifying of oils and chelating inorganic soils. The cleaner can also have agents for surfactants for emulsifying, wetting and penetrating, alkaline builders for neutralizing water hardness interference, corrosion inhibitors, etc. Alkaline cleaning is often followed by an acid rinse to neutralize the adhering alkaline material and remove non-soluble precipitates formed by reaction with the alkaline material. A mild alkaline cleaner has a pH of about 9.5 to 10.0, a strong alkaline cleaner will have a pH of 13.0.

Alloy–A solid solution where there is a stable mixture of the materials.

Altered region (ion bombardment)–The region near the surface which has been altered by the physical penetration of the bombarding species or by "knock-on" lattice atoms. In the extreme case this can lead to the amorphorization of the region. See *Near-surface region.*

Alternating ion plating (film deposition)–A repetitious process where a few monolayers of condensable film material is deposited and then the surface is bombarded followed periodically by more deposition and more bombardment. Also called *pulsed ion plating*.

Alumina (substrate)–Aluminum oxide (Al_2O_3). Alumina substrates are usually in the form of sintered material with some amount (4-15%) of silica glassy phase.

Aluminize–The process of depositing aluminum on a surface from a liquid or vapor.

Aluminize–The process of reacting a surface with aluminum to form an aluminum alloy or intermetallic phase.

Ambient conditions (vacuum technology, contamination control)–Conditions such as pressure, air composition, temperature, etc., that are present in the processing area.

Amine–Any one of a group of organic compounds derived from ammonia (NH_3) by replacement of one or more hydrogen atoms by organic radicals.

Ammonia (NH_3)–A chemical precursor vapor for nitrogen that is easier to decompose than is N_2.

Amorphous (crystallography)–A material without a periodic structure that would be revealed by x-ray diffraction. This is typically a grain size of less than about 30 Å.

Ampere (A)–Electrical current of one coulomb (1.6×10^{19} electrons) per second. Also called an *Amp*.

Amphoteric material–A material that can either gain or lose an electron (i.e., act as either an acid or a base) in a chemical reaction. Example: aluminum can form Al_2Cu or Al_2O_3.

Amorphous (crystallography)–Material with a grain size so small (<30 Å) that the x-ray diffraction pattern does not show any crystallinity. See *Glassy.*

Angle-of-incidence (film formation)–The angle of impingement of the depositing adatom flux as measured from the normal to the surface.

Angle-of-incidence effect (film growth)–The effect of angle-of-incidence of the adatoms on the development of a columnar morphology.

Angstrom (Å)–A unit of length equal to 10^{-10} meters or 0.1 nanometer.

Anhydrous (cleaning)–Without water. Example: anhydrous (absolute) alcohol.

Anion (electroplating)–An ion that is negatively charged and will move toward the anode.

Anisotropy, film properties (film formation)–Properties that differ in different direction in the plane of the film. Often due to anisotropy in the flux of depositing material or anisotropy in the bombardment during deposition.

Annealing–Reducing the internal stress of a material by raising its temperature (annealing temperature of metals; strain point of glasses) to the point that atoms can move so as to relieve the stress or other thermodynamic differences.

Anode–The positive electrode in a gas discharge or electroplating bath.

Anode-to-cathode ratio (electroplating)–The ratio of the surface area of the anode to that of the cathode.

Anodic arc, plasma (plasma technology)–An arc vaporization source where the vaporized material originates from a molten anode electrode. Also called a *distributed arc*. See *Arc source*.

Anodic cleaning (cleaning)–Cleaning a surface by removing (off-plating) material from the anode in an electrolytic cell. Also called *electrolytic cleaning*. Called *electrolytic pickling* if the solution is acidic.

Anodic etching–Roughening or exposing grain structure by anodic dissolution (off-plating) in an electrolytic cell.

Anodization–The electrolytic conversion of an anodic surface in an electrolysis cell or oxygen plasma (plasma anodization) to an oxide. Example: aluminum anodization.

Anodize, barrier–A non-porous anodic oxide that can be formed on materials such as aluminum, titanium, niobium. The thickness of the oxide is proportional to the anodizing voltage applied.

Anodize, porous–A porous anodic oxide that is formed in an electrolytic bath that corrodes the oxide as it is being formed thus giving porosity in the oxide and allowing a thick oxide layer to be formed. Generally the porous coating is sealed (expanded) by hydration in a hot water bath.

Antiferromagnetic–A material in which the electron spins are ordered in an antiparallel arrangement such that there is zero magnetic moment. Example: Cr.

Antioxidant–A substance added to a plastic to slow the degradation by oxidation.

Antireflection (AR) coating (ARC) (optics)–A film structure designed so that there is reduced reflection over a region of the spectrum but rather all radiation in that spectral region is transmitted into the substrate.

Antiseize compounds (vacuum technology)–Material applied to a surface to prevent cold welding and galling. Example: silver-plated stainless steel bolts. See *Lubricant, vacuum*.

Antistatic agent–Chemical substances which increase the surface conductivity of plastic materials and are used to prevent surface charge buildup. Often they are ionic materials which absorb water to become conductive.

Applied bias (PVD technology)–An electrical potential applied from an external source. See *Bias*.

Aqua regia (cleaning)–A mixture of hydrochloric acid and nitric acid in a ratio of 3:1.

Aqueous solution–A solution where water is the solvent.

Aqueous cleaning–Water-based cleaning such as mixtures of water, detergents, and other additives that promote the removal of contaminants.

Arc–A high-current, low-voltage electrical discharge between two electrodes or between areas at different potentials. See *Arc source*.

Arc, gaseous–An arc formed in a chamber containing enough gaseous species to aid in establishing and maintaining an electrical arc. See *Vacuum arc*.

Arc, vacuum–An arc formed in a vacuum such that all of the ionized species originate from the arc electrodes. See *Gaseous arc*.

Arc source vaporization–The vaporization of a material from a cathodic or anodic electrode under high current-low voltage conditions for PVD processing.

Arc source, anodic arc–An arc vaporization source where the vaporized material originates from the anode surface which is liquid. Also called a *distributed arc source.*

Arc source, cathodic arc–An arc vaporization source where the vaporized material originates from the cathode surface which is usually solid.

Arc source, filtered–An arc vaporization source designed to filter out the macros, generally by deflecting the plasma. See *Plasma duct, Macros*.

Arc source, random arc–Cathodic arc where the arc is allowed to move randomly over the cathode surface.

Arc source, steered arc–A cathodic arc where the arc is moved over the surface under the influence of a magnetic field.

Arc cleaning (plasma spraying) (cleaning)–The use of a cathodic arc to clean and etch (roughen) a surface prior to deposition.

Arc suppression–Techniques for quenching an arc before it becomes too destructive. These include: shutting-off the power or introducing a voltage pulse with an opposite polarity.

ARC vaporization–Vaporization of a solid (cathodic) or liquid (anodic) electrode material using a vacuum or gaseous arc. Characterized by high ionization of the vaporized material. Also called *arc evaporation.*

Arc-wire spray–A thermal spray process where the tip of a wire(s) is melted in an electric arc and the molten material is propelled to the substrate by a gas jet.

Archival samples–Samples retained after a specific portion of processing has been performed to allow comparison with material at a later stage or after being placed in service. See *Control samples, Shelf samples*.

Argon (sputtering)–An inert gas used for sputtering because it is relatively inexpensive compared to other inert gases and has a reasonably high mass (40 amu).

Aromatic solvents (cleaning, topcoats, basecoats)–Solvents based on benzene-ring molecules such as benzene, xylene and toluene. Used as diluents in acrylic lacquers.

Arrhenius equation–A equation relating a rate, such as a chemical reaction rate, to an activation energy and the temperature.

ASA flange (vacuum technology)–A flange for joining tubing that has a specific bolt pattern for each diameter.

Ashing (cleaning)–Reducing a material to non-volatile residues (ash) by high temperature or plasma oxidation.

Aspect ratio (substrate)–The ratio of the depth to the width of a feature such as a via (hole) or trench in a multilayer film structure.

Asperity (surface)–A small protuberance from a surface. It may be of the bulk material or be an inclusion.

ASME Boiler and Pressure Vessel Code (vacuum technology)–The American Society of Mechanical Engineers code by which the material, material thickness, design and construction methods are specified for pressure vessels. Since a vacuum chamber is a pressure vessel the code is often used in specifying the construction of vacuum chambers.

As-received material (manufacturing)–Material that enters the processing sequence. The material may be from an outside supplier or from a previous processing sequence. See *Process Flow Diagram; Inspection, incoming*.

Asymmetrical AC (electroplating)–Where the magnitude of the voltage in one polarity of a alternating current (AC) voltage is different than the magnitude in the other polarity.

Atom–The basic unit of a chemical element.

Atomic Force Microscope (AFM) (characterization)–A stylus surface profilometer which measures the deflection of a probe mounted on a cantilever beam. The AFM can be operated in three modes: contact, non-contact and "tapping" mode. Also called the *Scanning Force Microscope* (SFM).

Atomic mass unit (amu)–The atomic mass unit is defined as 1/12 of the mass of the ^{12}C isotope. Also called the *Unified atomic mass unit* (u) . One amu = 1.66×10^{-24} g.

Atomic peening (film formation)–The continuous or periodic bombardment of a depositing film with high energy atoms or ions to densify the depositing film material. Atomic peening tends to introduce compressive stress into the surface.

Atomically clean surface–A surface that does not contain an appreciable fraction of a monolayer of foreign material on the surface. Very difficult to obtain and retain.

Auger electron emission–The emission of electrons from an excited atom, which have a characteristic energy due to specific transition between orbital states in the atom.

Auger Electron Spectroscopy (AES) (characterization)–A surface analytical spectroscopy technique that uses energetic electrons as the probing species and Auger electrons as the detected species.

Augmented plasma (plasma technology)–A plasma that has had electrons injected from an outside source to enhance ionization.

Aurora Borealis coating (decorative coating)–Coating with a rainbow of colors formed by depositing films or anodizing surfaces to give colored interference patterns.

Autocatalytic plating–See *Electroless plating.*

Auxiliary plasmas (plasma technology)–A plasma established in a processing system to assist is some aspect of the processing separate from the main processing event. Example: plasma cleaning in a vacuum deposition system, plasma activation of the reactive gas near the substrate in a reactive magnetron sputter deposition system.

Avogadro's Number–The number of molecules contained in one mole (gram-molecular-weight) of a substance. The value is 6.023×10^{23}.

Availability, reactive gas (film formation)–The availability of the reactive gas over the surface of the film being deposited. Since the surface of the film is continually being buried, reactive gas availability is an important parameter in reactive deposition.

Avoirdupois (a) weight system–Common pound and ounce system where 1 ounce (oz) (a) = 28.4 grams and 1 pound (a) = 16 oz (a). See *Troy weight system.*

Azeotropic mixture (cleaning)–Solvent mixture where the vapor has the same composition as the liquid.

Back-diffusion (vacuum technology)–Flow of vapor in a direction opposite to that of the flow of gas being pumped. Occurs in the molecular flow range. Also called *backstreaming*.

Back-end (semiconductor technology)–Final processing such as dicing, wire bonding, encapsulation, test, assembly packaging, etc. See *Front end*.

Back-scattering–Scattering of particles in a direction counter to that of the main particle flow.

Backfill (vacuum technology)–Raising the system pressure with a specific gas (e.g., backfill with dry gas). See *Venting*.

Backing plate (sputtering target)–The plate that the target material is bonded to that allows mounting to the cooling portion of the sputtering target assembly.

Backing pump (vacuum technology)–A vacuum pump used to keep the discharge pressure of a high vacuum pump below some critical value. The backing pump may be also used as a roughing pump. Also called a *forepump.*

Backpressure (vacuum technology)–The pressure in an exhaust system that impedes the flow of gas through the system.

Backstreaming (vacuum technology)–Movement of gases or vapors from the high pressure to the low pressure region of a vacuum system. Also called *back-diffusion*.

Baffle (vacuum technology)–A system of surfaces designed to minimize back-streaming either by condensation or reflection. Also called a *trap*.

Baffle (PVD technology)–A system of surfaces to prevent a cold surface from seeing the thermal radiation from the processing chamber.

Baffle source (evaporation; PVD technology)–An evaporation source in which the vapor must collide with several hot surfaces before it can leave the source. Used to evaporate materials such as selenium and silicon monoxide which vaporize as clusters of atoms or molecules.

Bag filter (vacuum technology)–Mechanical filter to prevent particulates from entering the vacuum pumping system.

Bag-check (vacuum technology)–Covering a vacuum system with a bag filled with helium to measure the total real leak rate into the system.

Bake-out (vacuum technology)–The heating of a vacuum system to a high temperature (i.e., 400°C) during pumping to accelerate outgassing and desorption from materials and surfaces in the vacuum system.

Baking, vacuum (cleaning)–Heating of a material at an elevated temperature for a period of time sufficient to reduce volatile constituents such as water, solvents and plasticizers to an acceptable level. Care must be taken not to heat the material to a temperature at which it will decompose. The necessary time and temperature is generally determined using weight-loss or mass spectroscopic analysis.

Baking soda (cleaning)–Sodium bicarbonate. Used as a water-soluble mild abrasive.

Ball bond–A wire bond to a film consisting of a ball formed on the tip of a wire that is bonded to the surface under heat and pressure (thermocompression bonding) or under pressure and ultrasonic scrubbing (ultrasonic bonding). See *Wire bond*.

Ballast tank (vacuum technology)–A large volume that can be continuously pumped which is used to assist in rapid roughing by opening the much smaller volume of the deposition chamber to a ballast tank for the initial rough pumping.

Ballast valve (vacuum technology)–A valve in or just before the mechanical pump that can be used to allow dilution of the pumped gas with dry gas to ensure that vapors in the pumped gas do not condense during compression in the mechanical pump. The ballast valve can also be opened automatically to allow the foreline portion of the vacuum pumping manifold to return to ambient pressure in case the mechanical pump stops because of a power failure. This avoids suck-back. See *Suck back*.

Ballast orifice (vacuum technology)–An orifice upstream of the mechanical pump that can be used to allow dilution of the pumped gas with dry gas to ensure that vapors in the pumped gas do not condense during compression in the mechanical pump. The ballast orifice also allows the foreline portion of the vacuum pumping manifold to return to ambient pressure in case the mechanical pump stops because of a power failure or a broken belt. This avoids suck-back.

Band-pass filters (optical coatings)–Optical coatings that allow a band of specific wavelengths to pass through and others to be reflected or absorbed. See *Heat mirror, Dichroic coatings*.

Banding (PVD technology)–A striped pattern on large-area substrates or webs due to variation in film thickness, morphology or composition across the width of the substrate.

Bar (pressure)–Pressure equal to 10^5 Pascals. 1 bar = 0.98692 atmospheres = 750.06 Torr. Pressure unit commonly used in Europe. A millibar is 0.001 bar.

Barrel plating (electroplating, PVD technology)–Plating objects that are loose inside a rotating grid structure (cage or barrel) so that they are tumbled and completely covered. See *Fixture*.

Barrier film (diffusion, permeation)–A film used to reduce the diffusion into a surface or through a film. Example: TiN underneath aluminum metallization on silicon to prevent diffusion of Al into the silicon on heating; aluminum film on a polymer web to reduce water permeation through packaging material.

Base–Any chemical species capable of accepting a proton (hydrogen ion) from another species. (Example: OH^-). An acid yields hydrogen ions (H^+) by reaction with the solvent while a base forms hydroxyl ions, OH^-. See *Acid*.

Base pressure (vacuum technology)–A specified pressure for the system to begin the next sequence in the processing. See *Pump-down time*.

Basecoat (PVD technology)–A film, often a polymer, that is applied to a surface to produce a smooth surface (flow coat), to seal-in material that will outgas during vacuum processing or to provide a "glue-layer" for adhesion.

Baseplate–The large-area stationary surface, usually horizontal, on which a moveable vacuum chamber seals and which contains many of the feedthroughs into the system. See *Collar*.

Basic surface (film formation, adhesion)–A surface capable of supplying an electron to an atom on its surface. See *Acidic surface*.

Batch–A group of substrates processed together in a fixture.

Batch processing system–A system where the processing chamber is opened to the ambient each time the fixture is placed into or removed from the chamber. Also called a *direct-load system* (preferred).

Bayard–Alpert gauge (vacuum technology)–A hot cathode ionization gauge using a fine-wire ion collector to minimize x-ray effects in the gauge.

Bead blasting, glass (cleaning)–Subjecting a surface to bombardment by glass beads entrained in a high velocity gas flow to abrasively clean the surface.

Beam density–Particle flux (particles per cm^2) in the beam.

Beam intensity–Power density of the beam (watts per cm^2).

Beamsplitter (optics)–An optical filter or reflector that reflects some of the incident radiation and transmits the rest.

Belljar (vacuum technology)–A moveable glass or metal vacuum chamber that is generally cylindrical with a domed top that seals to a baseplate. Most often removed by lifting from the baseplate.

Bellows, metal (vacuum technology)–An expandable tube of metal that is used to allow alignment of flanges, isolation from vibration, or motion in a linear direction.

Bend test (adhesion)–An adhesion test where the coated substrate is bent around a radius and the coating is observed for spallation from the substrate. See *Adhesion tests*.

Beta particles–Electrons from radioactive sources.

Beta test (semiconductor processing)–Evaluation of equipment by an OEM (original equipment manufacturer) under production conditions to determine what changes should be made before supplying the final version of the equipment to the user.

Bias (statistics)–A systematic error that contributes to the difference between the mean of the measurement and an accepted reference or true value.

Bias, applied (PVD technology)–An electrical potential applied from an external source.

Bias, electrical (PVD technology)–The electrical potential between one surface or region and another surface or region.

Bias, magnetic (PVD)–Magnetic field in the vicinity of the substrate during deposition to affect the structure and orientation of deposited magnetic films.

Bias, self (plasma technology)–An electrical potential on a surface generated by the accumulation of excess electrons (negative self-bias) or positive ions (positive self-bias). See *Sheath potential*.

Bias sputtering–Sputter deposition with a bias on the substrate to accelerate ions to the surface during deposition. See *Ion plating*.

Biaxial orientation (BO) (substrate, polymer web)–The process of stretching a plastic film (usually at elevated temperatures) in both the machine and transverse directions so as to achieve similar tensile, modulus and elongation properties in the film.

Binding energy–The strength of the chemical bond between atoms.

Bit (semiconductor)–A unit of information represented by a change of state (i.e., on then off). See *Byte*.

Bit density (semiconductor)–The number of bits (information storage) per unit area on a silicon chip (or magnetic tape).

Black body (radiation)–A surface that absorbs all radiation of any wavelength that falls on it. The surface will have an emittance of unity.

Black body radiation–The characteristic radiation from a blackbody surface at a specific temperature.

Black breath test (cleaning)–Condensation of moisture from a person's breath on a cleaned surface. Uniform nucleation indicates a uniformly clean surface (if the contamination is not hydophillic).

Black sooty crap (BSC)–Ultrafine particles formed by vapor phase nucleation in a gaseous environment. See *Soot; Ultrafine particles*.

Blanket metallization (PVD technology)–Metallization over the whole surface. See *Selective metallization*.

Bleb (glass)–A bump on the surface of glass caused by a bubble or inclusion in the glass.

Bleed (vacuum technology)–The continuous admission of a small amount of gas into a vacuum or plasma system.

Blister (adhesion)–An enclosed separation of a coating from the substrate.

Blocking (web coating)–When the film sticks to itself in the wound condition on the roll.

Blow hole (basecoat, topcoat)–A void in a flow coating formed by outgassing during heating before the coating is cured.

Blow-off (cleaning)–A method of cleaning particulates from a surface using a high velocity stream of clean gas. When blowing-off the surface of an insulator the gas should be ionized to prevent static charge buildup on the insulating surface.

Blower (vacuum technology)–A low-compression mechanical, compression-type vacuum pump. Example: roots blower.

Boat source (evaporation)–An evaporation source where the charge is contained in a cavity in a surface. Generally the boat is of tungsten, tantalum or molybdenum and is heated resistively. The cavity may be coated with a ceramic so that the molten charge does not come into contact with the metal. See *Evaporation source*.

Body covering (cleaning)–The coat, head covering, face covering, shoe covering, gloves, etc., used to contain particulate contamination generated by a persons body and cloths.

Boiling point–When the vapor pressure of the material is the same as the ambient pressure. Example: at sea level the boiling point of water is 100°C.

Boiling beads (evaporation)–Solid masses added to a liquid to prevent splattering and spitting during boiling or evaporation. Example: tantalum shot in molten gold to prevent spitting by vapor bubbles rising through the molten gold.

Boltzmann's constant (k)–The ratio of the Universal Gas Constant to Avogadro's number. The constant (k) in the equation E = 3/2 kT which gives the mean energy (E) of a free particle at a temperature T (K). $k = 1.38 \times 10^{-16}$ erg/deg (K).

Bombardment-enhanced chemical reactions (film formation)–Chemical reactions on a surface that are enhanced by bombardment by high energy atomic-sized particles. The effect is due to heating, dissociation of adsorbed species, production of electrons, etc. Important effect in reactive deposition, PECVD, plasma etching and reactive ion etching.

Bond energy–The Heat of formation of a molecule from its constituent atoms.

Bondability (semiconductor processing)–The ease with which a wire can be attached to the surface.

Bonding (sputtering target)–The attachment of the sputtering target to the backing plate using a technique that gives good thermal contact.

Bonding pad–An area of film where a contact such as a wire is to be bonded usually under heat and pressure (Example: thermocompression bond). Substrate under the film is put under significant stress.

Booster pump (vacuum technology)–A pump used between the high vacuum pump (particularly the diffusion pump) and the backing pump in order to increase the throughput in the medium vacuum range and decrease the volumetric flow through the backing pump. Example: diffusion pump exhausts into a roots blower (booster pump) then into an oil-sealed mechanical pump. See *Vacuum pump*.

Booties (contamination control)–Shoe coverings used in a cleanroom.

Boronize (substrate)–The process of diffusing boron into a surface region containing Mo, Cr, Ti, etc., so as to form a surface layer (case) containing boride compound particles dispersed through the layer.

Boundary layer (cleaning)–The layer of stagnant fluid next to a surface through which cleaners must diffuse to reach the surface. See *Agitation*.

Boundary layer (electroplating)–The layer of stagnant fluid next to a surface through which ions must diffuse to reach the surface. See *Agitation.*

Box coater (deposition chamber)–A direct-load deposition chamber in the form of a flat-sided box, often with gussets, with one or more sides being a door. See *Deposition system*.

Boyle's Law–For an ideal gas at a fixed temperature the product of the volume of the gas and its pressure is equal to a constant.

Braze alloy (vacuum technology)–A metallic alloy that melts above about 450°C and is used to join two materials together.

Bright dip (surface)–A chemical treatment that tends to preferentially etch the high points on a surface thus increasing the smoothness of the surface. Example: 10% HCl on aluminum.

Brightness–One component of color. The component of color that gives the perception of intensity. Also called *luminance*. See *Color*.

Brittle fracture (adhesion)–Fracture of a material with little or no plastic deformation.

Brittle material–A material that allows little or no plastic deformation before failure. Generally such a material has a low fracture toughness.

Brown-out–When the power line voltage drops below a specific voltage. A brown-out can affect the operation of electrical gear such as motors, electronics, etc.

Brush plating (electroplating)–Plating where the anode is a moveable electrode and the electrolyte is held in an absorbent material (swab) on the anode. The part to be coated is made the cathode.

Bubbler (agitation)–Perforated pipe distributor for fluids or gases used in the bottom of fluid tanks for agitation. Also called a *sparger*.

Buckles (web coating)–Ridges of film that extend across the roll or around the roll of film material.

Buffer layer (cleaning, etching)–A layer of material which has properties or crystal structure, intermediate between the film and the substrate materials and allows gradation of properties between the two materials. See *Compliant layer*.

Buffered solutions (cleaning)–A chemical solution formulated to minimize the change of hydrogen ion concentration in the solution due to chemical reactions.

Bulkhead mounting (vacuum technology)–When a chamber is mounted through a wall such that the chamber opening is on one side and the pumping plumbing is on the other side of the wall. This design ensures that persons working on the pumping system do not contaminate the processing environment of the opening side. See *Pass box*.

Bulk getter (vacuum technology)–A mass of material that retains gases that diffuse into it. See *Getter*.

Bunny suit (cleaning)–Body covering that covers the head, neck, torso, legs and feet.

Burnishing–Smearing a soft metal either by mechanical contact with a smooth surface such as steel balls, or by the use of a mild abrasive. Examples: barrel burnishing, vibratory burnishing.

Burr–A thin protruding piece of metal along an edge that is left after a forming process.

Byte (b) (semiconductor)–An association of binary bits that act as a unit in a computer.

Calcium carbonate ($CaCO_3$) (cleaning)–Used as a polishing/cleaning abrasive. Insoluble in water, soluble in acids. Also called *chalk*.

Calibrated leak–A leak which has a known leak-rate (Torr-liters/sec) for a specific gas under specific conditions. Used to calibrate leak detectors.

Calibration–To determine by comparison to a standard the absolute value of each scale reading of a sensor device. Comparison must be done in a specified manner under specified conditions. See *Standards, primary; Standards, secondary*.

Calibration log–The document describing when a unit was calibrated, by what method and the name of the person that did the calibration.

Canted-spring seal (vacuum technology)–A slit tubular seal which has the restoring force provided by a canted coil spring inside the tube.

Capacitance manometer (vacuum technology)–A vacuum gauge that uses the deflection of a diaphragm, as measured by the changing capacitance (distance) between surfaces, as an indicator of the pressure differential across the diaphragm, the pressure on one side being a known value. See *Vacuum gauge*.

Capacity, pump (vacuum technology)–The amount of a specific gas that a capture pump, such as a cryopump, can contain and still pump effectively. When this value is exceeded the pump is ineffective and must be regenerated. See *Regeneration.*

Capillary action–The combination of adhesion and cohesion that cause fluids to flow or rise between closely spaced surfaces.

Capillary waves (substrate)–Periodic waviness on a polished surface. See *Orange peel*.

Capture pump (vacuum technology)–A vacuum pump that captures and holds the gases and vapors being pumped. See *Vacuum pump*.

Carbides, metal (corrosion)–Carbon-metal compounds that can be formed in some alloys in the Heat Affected Zone (HAZ), during welding, that can give galvanic corrosion problems. See *Stainless steel, Low carbon steel*.

Carbon dioxide (CO_2), liquid (cleaning)–Liquified carbon dioxide used as a solvent. See *Green cleaning*.

Carbon dioxide (CO_2), snow (cleaning)–Solid carbon dioxide that is used to abrasively clean a surface and is formed by expansion and cooling of a jet of compressed carbon dioxide gas.

Carbonyl (carbonyl group)–The radical (C=O). Example: $Mo(CO)_6$.

Carbonitriding (substrate)–Hardening by diffusion of both carbon and nitrogen into a metal surface to form both carbide and nitride phases dispersed in the surface region. See *Carburizing, Nitriding*.

Carburizing (substrate)–The process of diffusing carbon into a surface region of an alloy containing Cr, Ni, Mo to form a carbide phase and give dispersion strengthening.

Carcinogenic (chemical)–A chemical that has been shown to cause cancer in mice. See *Mutagenic*.

Carrier gas (CVD)–Gas used to decrease the concentration of reactive gases in CVD reactions without changing the total pressure or to entrain and carry vapors into the reaction chamber. Also called a *diluent gas.*

Cascade rinse (cleaning)–Rinsing using a series of containers (tanks) having increasingly pure water. Water flows over the lip of one container into the next container having lower purity water. The surface being rinsed goes from the lower purity to the higher purity rinse tank. Also called *counterflow rinse*. See *Spray rinse*.

Case (substrate)–A hardened surface region that can extend many microns into the surface.

Case hardening–Surface hardening by forming a dispersion-strengthened surface layer (case) of appreciable depth by one of several techniques.

Catalyzed reaction–A chemical reaction whose rate is increased by a material that is not consumed in the reaction.

Cathode–The negative electrode in a gas discharge or electroplating bath.

Cathode spot (plasma technology)–The area on the cathode, under normal glow discharge conditions, in which the current is concentrated. As the current increases the spot becomes bigger in order to maintain a constant current density in the cathode spot. In the abnormal glow discharge the cathode spot covers the whole cathode area.

Cathodic arc (PVD technology)–A vaporization source where the vaporized material originates from a high current density arc on the cathode surface which is usually solid. See *Anodic arc.*

Cathodic cleaning–Cleaning in an electrolytic cell where the surface to be cleaned is the cathode. See *Anodic cleaning*.

Cation (electroplating)–An ion that is positively charged and will move toward the cathode. See *Anion*.

Cationic detergent (cleaning)–A detergent that produces aggregates of positively charged particles with colloidal properties.

Cavitation (cleaning)–Formation of vapor-filled voids (bubbles) in a fluid under tensile stress. The voids grow to a size determined by the surface tension of the fluid and then collapse. If the voids are in contact with a surface the collapse produces a jet of fluid which can clean the surface and cause cavitation erosion of the surface. See *Ultrasonic cleaning*.

Ceiling (safety)–The exposure limit to which a worker must not be exposed to even instantaneously as set by OSHA. See *Threshold limit, Time weighted average, Short term exposure limit*.

Centigrade temperature scale–A temperature scale in which the freezing point of water is taken as 0°C and the boiling point of water, under standard pressure, is taken as 100°C. Also called the *Celsius temperature scale*. See *Temperature scale*.

Cerium oxide (CeO_2)–Fine polishing compound used to polish glass.

Chalk (cleaning)–Calcium carbonate ($CaCO_3$). Used as a polishing/cleaning abrasive. Insoluble in water, soluble in acids.

Chamber, deposition–See *Deposition system*.

Channeling (ion bombardment)–The preferential movement of an energetic ion or atom along the open region between crystallographic planes in a solid crystal.

Characterization, film–Determining the properties of a film using specified characterization techniques.

Characterization, extensive–Determining some film properties, such as crystallography, gas content, chemical concentration gradient, etc., which will take a significant period of time.

Characterization, first check–Determining some film properties such as color, after the fixture has returned to ambient pressure but before the substrates have been removed from the fixture. See *Position equivalency*.

Characterization, functional–Characterization of the properties of the film that can or will be used in the final product. Example: optical reflection.

Characterization, in situ–Determination of some film properties, such as thickness, optical properties, etc., during the deposition process or before the system has been returned to ambient pressure.

Characterization, non-destructive–Determination of some film properties, such as thickness, optical properties, etc., without affecting the film in a detrimental manner.

Characterization, rapid feedback–Determining some film properties such as sheet resistivity, thickness or chemical composition, soon after the substrates have been removed from the fixture. See *Position equivalency*.

Charcoal, activated (vacuum technology)–See *Activated carbon*.

Charge (evaporation)–The material to be vaporized that is placed in a thermal vaporization source.

Charge exchange (plasma)–When a positive ion gains an electron from a neutral atom. If the ion has a high energy the process produces a high-energy neutral and a low-energy ion.

Charge separation–When two atoms, molecules or surfaces are separated and one material has excess electrons and the other has a deficiency of electrons. This situation can cause arcing. See *Exoemission.*

Charging, hydrogen (cleaning)–When hydrogen is introduced into a surface by a chemical, electrochemical or implantation action so as to form a high chemical gradient between the surface region and the bulk of the material. Example: electroplating of chromium introduces large amounts of hydrogen into the chromium, acid cleaning of some metal surfaces introduces hydrogen into the surface.

Charles Law–For an ideal gas at a constant pressure the volume of a fixed mass of gas varies directly with the absolute temperature.

Chelating agents (cleaning)–An organic compound that reacts with metal ions in solution and prevents them from reacting with other ions and being precipitated as an insoluble compound. Can pose a water pollution problem. Example: chelating agents include Ethylene Diamine Tetraacetic Acid (EDTA), amine compounds and various polymers.

Chemical bond–The strong attractive forces that exist between atoms or molecules due to electrical effects within and between atoms and molecules.

Chemical bonding, covalent–The chemical bond that is formed between two atoms which each contributes one electron. If the electrons are shared unequally it is a covalent polar bond. Also called *electron pair bond.*

Chemical bonding, ionic–The chemical bond that is formed between atoms which have opposite electrical charges due to the transfer of an electron from one to the other. Example: NaCl.

Chemical bonding, metallic–The chemical bond that results from the immersion of the metallic ions in a "continuum" of freely-moving electrons.

Chemical bonding, polar–The chemical bond that results between two atoms or molecules which are oppositly polarized.

Chemical bonding, Van der Waals–The chemical bond that results from the dipole interaction between two atoms or non-polar molecules. Also called *dispersion bonding.*

Chemical conversion–The formation of a surface layer due to chemical reaction with a selected material. Examples: chromate conversion, phosphate conversion.

Chemical deposition–The deposition of a metal film by precipitation where another metal ion displaces the depositing atom in a solution of the metal salt. Example: chemical silvering.

Chemical Equivalent Weight–Gram atomic (molecular) weight divided by the valence of the ion. Also called *gram equivalent weight*. See *Mole*.

Chemical etch-rate test (characterization)–The rate (Angstroms per minute or mass per unit area per minute) at which material is removed by chemical etching.

Chemical etching (cleaning)–The removal of material by chemical reaction with a fluid (wet chemical etching) or vapor (vapor etching) to produce a soluble or volatile reaction product. The etch rate is affected by the density, porosity and composition of the film.

Chemical hoods–Enclosed, ventilated (air flow >100 ft/min) region for performing chemical processes and isolating the processes from other processes.

Chemical polishing–Chemical removal of the high points on a surface.

Chemical potential–The chemical concentration difference between two regions.

Chemical pumping–The removal of gas by having it react it with a material to form a compound having a low vapor pressure. Also called *gettering*. See *Getter pumping, Getters, Ion pumping*.

Chemical roughening–Surface roughening by the preferential attack of features such as crystallographic planes, grain boundaries and lattice defects.

Chemical silvering–The deposition of silver from solution by the reduction of a silver-containing chemical. Example: used in coating backsurface mirrors and vacuum flasks.

Chemical solution, strength of–See *Normal solution, Molar solution, Percent solution, Specific gravity*.

Chemical strengthening, glass (substrate)–Placing the surface of the glass in compression by replacing small ions (e.g. Na) with larger ions (e.g. K) in the surface region by diffusion.

Chemical Vapor Deposition (CVD)–The deposition of atoms or molecules by the reduction or decomposition of a chemical vapor species (precursor gas) which contains the material to be deposited. Example: silicon (Si) from silane (SiH_4). See *Vapor Phase Epitaxy, Decomposition reaction (CVD), Reduction reaction (CVD), Disproportionation reaction (CVD)*.

Chemical vapor precursor (CVD, reactive deposition)–A gaseous chemical species that contains the species to be deposited. Example: Silane (SiH_4) for silicon, methane (CH_4) for carbon.

Chemical-mechanical cleaning (cleaning)–Combining chemical etching with mechanical abrasion.

Chemical-mechanical-polishing (CMP) (semiconductor processing)–A combination of chemical polishing and mechanical polishing that is used to planarize a surface.

Chemisorption–The retaining of a species on a surface by the formation of strong chemical bonds (>0.2 eV) between the adsorbate and the adsorbing material. See *Physisorption*.

Chip (electronic)–A discrete device such as a transistor, capacitor, resistor, etc., on a brittle substrate such as silicon or ceramic.

Chip (flaw)–A region of a brittle material that is missing due to fracture, usually due to handling. The chip can be an edge chip or a surface chip.

Chip (semiconductor)–One of many discrete semiconductor devices on a silicon wafer. As-fabricated each wafer contains many chips and is "diced" to create individual chips.

Chlorinated solvents (cleaning)–Solvents containing carbon and chlorine such as Trichloroethylene (TCE), Methylene chloride (MEC), Perchloroethylene (PCE) and 1,1,1 trichloroethane (TCA). Very effective solvents but regulated because of health and environmental concerns. Example: carbon tetrachloride (CCl_4) a fully chlorinated solvent. See *Chlorofluorocarbon (CFC) solvents, Hydrochlorofluorocarbon (HCFC) solvents*.

Chlorofluorocarbon (CFC) solvents (cleaning)–Solvents containing chlorine and fluorine. Used in removing non-polar contaminants such as oils. Effective solvents but regulated because of health and environmental concerns. Example: CFC-11 (CCl_3F), CFC-12 (CCl_2F_2) and CFC-113 ($CF_2ClCFCl_2$). See *Chlorinated solvents, Hydrochlorofluorocarbon (HCFC) solvents*.

Chromate conversion–Treatment of a metal surface with a hexavalent chromate solution to form a protective (corrosion resistant) metal-chromate surface layer.

Chromize–The process of reacting a metallic surface with chromium to form a high-chromium alloy surface region.

Cladding–The covering of a surface by a solid layer of a second material and then bonding the two together by temperature and pressure.

Class, cleanroom (cleaning)–Number of airborne particles greater than 0.5 micron in size per cubic foot (actual number i.e., Class 10 = 10 particles per cubic foot) or per cubic meter (logarithm of number to the base 10 or M) (Class 10^3 M2.5).

Clean area, soft-wall (cleaning)–A cleanroom in which the area is defined by hanging plastic drapes and the air flow enters through the ceiling and exits under the drapes (downflow).

Clean bench (cleaning)–An enclosed bench which uses a laminar flow of mechanically filtered air to provide a working area with a reduced number of particulates.

Cleanroom (cleaning)–A processing area (room) in which the particulate contamination has been reduced to a specified level by mechanical filtering. Generally the filtered air enters through the ceiling and exits through the floor or lower sidewalls. See *Class, cleanroom.*

Cleanroom, materials for (cleaning)–Materials that do not introduce particulates or vapors into the clean area. Example: non-linting cloth and paper, stainless steel rather than vinyl furniture covering, ink pens rather than carbon pencils.

Cleaning (cleaning)–Reduction of the amount of contamination on a surface to an acceptable level.

Cleaning, alkaline (cleaning)–A basic cleaner that cleans by saponifying oils. Alkaline cleaning is often followed by an acid rinse to neutralize the adhering alkaline material and remove nonsoluble precipitates formed by reaction with the alkaline material.

Cleaning, external (cleaning)–Cleaning done external to the deposition chamber.

Cleaning, gross (cleaning)–Cleaning process designed to remove all types of surface contaminants, generally by removing some of the underlying surface material.

Cleaning, in-situ–(cleaning)–Cleaning done in the deposition chamber.

Cleaning, plasma (cleaning)–Cleaning done using an inert or reactive gas plasma either as an external cleaning process in a plasma cleaner or as an *in situ* cleaning process in the deposition system. See *Glow bar*.

Cleaning, solvent (cleaning)–Cleaning using a solvent that takes the contamination into solution. See *Solubility test, Specific cleaning*.

Cleaning, specific (cleaning)–Cleaning process designed to remove a specific contaminant. Example: removal of a hydrocarbon contaminant by oxidation.

Cleaning, sputter (cleaning)–A gross, *in situ* cleaning process where the substrate surface is sputtered prior to the film deposition.

Cleaning, wipe-down (cleaning, vacuum technology)–Cleaning by wiping with a wet lint-free, low-extractables pad containing a solvent such as alcohol. The wet surface picks up particulates and the solvent takes contamination into solution. Anhydrous alcohol is often used as a wipe-down fluid since it will displace water and will rapidly vaporize.

Cleaning procedure, RCA (semiconductor processing)–A specific cleaning procedure designed to clean silicon wafers. A variation of the procedure is called the modified RCA cleaning procedure.

Cleaving (cleaning)–The process of introducing a fracture in a single-crystal material that follows a crystallographic plane. One method of producing a clean surface in vacuum.

Coarse vacuum (vacuum technology)–Vacuum in the range of atmospheric to about 10^{-3} Torr. Also called *rough vacuum* (preferred). See *Rough vacuum.*

Closed-loop system (cleaning)–A cleaning line where the cleaners and rinsing agents are recycled so that there is very little dilute liquid waste generated. Contaminants are in the form of solids on filters or as concentrated liquid wastes. See *Enclosed system.*

*Coat (*garment, cleaning)–Outer clothing used to contain particulates generated on the body by presenting a barrier to air flow away from the body using a closely-woven cloth or a solid fabric. Open at the bottom so particulates drop to the floor. See *Bunny suit.*

Coating–Term applied to overlayed material on a surface greater than several microns in thickness. See *Overlay, Thin film, Surface modification.*

Coefficient of adhesion–The ratio of the force needed to pull surfaces apart to the force used to force them together.

Coefficient of friction (vacuum technology)–The ratio of the force parallel to the direction of motion needed to start movement (static friction) or continue movement (dynamic friction), to the load applied normal to the direction of motion. The higher the coefficient of friction, the more likely the galling and generation of particulate contamination.

Coefficient of Thermal Expansion (CTE) (film formation)–The linear expansion (generally positive) as a function of increasing temperature.

Cohesion–The chemical bonding between like atoms in a bulk material.

Cohesive energy–The force (pounds/inch^2 or newtons/meter^2) needed to separate a bulk material and form two surfaces.

Coil source (evaporation)–A thermal evaporation source in the form of a coil, usually of stranded wire, that is wetted by and holds the molten evaporant material and allows deposition in all directions. See *Evaporation source.*

Coining (substrate)–Impressing a design into a surface by forcing a hardened die into the surface.

Cold cathode ionization gauge (vacuum technology)–An ionization-type vacuum gauge where the electrons for ionization are usually produced by a secondary electron emitting surface or a radioactive material. Often uses a magnetic field to increase the path length of the electrons.

Cold cathode–A non-thermoelectron-emitting cathode that emits electrons usually by secondary electron emission under ion bombardment or by radioactive decay. See *Field emission.*

Cold cleaning (cleaning)–Cleaning performed at room temperature.

Cold mirror (optics)–A thin film structure which reflects shorter wavelengths (typically visible) while transmitting longer wavelengths (infrared). See *Heat mirror.*

Cold trap (vacuum technology)–A baffle that operates by condensing vapors on a cold surface.

Cold welding–The bonding of metals at a low temperature generally due to removal or disruption of the oxides on the metal surfaces. See *Galling.*

Collar, feedthrough (vacuum technology)–A short metal cylinder on which feedthroughs are mounted and located between the baseplate and the belljar and provides a sealing surface for both the baseplate and the belljar.

Collimated sputter deposition (PVD technology)–Reduction of the non-normal flux from a sputtering target by using a honeycomb-shaped mechanical filter between the target and the substrate. Used to increase the throwing power in covering high-aspect-ratio surface features.

Colloids–Dispersion of small (< 200 microns diameter) particles in a second material.

Color–The optical property (generally using reflected wavelengths) of a surface that stimulates color receptors in the human eye. The perception of color is sensitive to the illumination used and the individual observing the color. Color is quantified using the parameters L*, a*, and b*, where L* is the luster or brightness of the coating, a* is the color content from green to red (wavelength and amplitude), and b* is the color content from blue to yellow (wavelength and amplitude). See *Brightness, Commission International de l'Eclairage (CIE)*.

Colorimetric imaging (characterization)–A method of locating pinholes in a film by reaction of the exposed substrate with a chemical to form a colored corrosion product that can be visually observed.

Columnar morphology (film formation)–The morphology that develops with thickness due to the development of surface roughness due to preferential film deposition on high points on the surface. The columnar morphology resembles stacked posts and the columns are not single grains. Also called *microcolumnar morphology*. See *Macrocolumnar morphology.*

Comets–The visual trail in the deposition system left by molten globules emitted from a thermal vaporization or arc vaporization source. See *Spits, Macros*.

Commission International de l'Eclairage (CIE) (International Commission on Illumination)–The organization that provides standards of color for its measurement and specification.

Comparative test (characterization)–A test to compare a film property to a standard or to previous results without providing an absolute value. Comparative tests are often used in production to ensure product reproducibility.

Complex ion (electroplating)–An ion composed of two or more ions or radicals each of which can exist independently.

Complexing (electroplating)–Attaching a metal ion to a larger ion so that its response to the electric field does not depend on the metal ion. Example: by complexing both lead and tin a Pb-Sn solder alloy can be electrodeposited.

Complexing agents (electroplating)–Chemical agents, such as cyanides, that are used for complexing.

Compliant layer (adhesion)–An intermediate layer that can distribute the stress that is applied and prevent high stress-loads at the interface. The compliant layer can be of a porous material or an easily-deformed material. See *Buffer layer*.

Composite material–A material composed of particles, precipitated grains, or fibers of one material dispersed in a matrix of another material. Example: fiberglass and dispersion strengthened steel.

Compound, chemical–Material formed when two or more elements combine to form a phase with a specific crystalline structure and a specific composition (with the possibility of some variability in elemental ratios). Example: SiO_2 and $SiO_{1.8}$ (silica and substoichiometric silica).

Compound-type interface (film formation)–When the interfacial material (interphase material) that has been formed during the deposition of A onto B along with subsequent diffusion and reaction, consists of a compound of A and B such as an oxide. See *Interface*.

Compression ratio (vacuum pump)–The ratio of the outlet pressure to the inlet pressure of a vacuum pump at zero flow using a specified gas.

Compressive stress, film (film formation)–A stress resulting in the atoms being closer together than they would be in a non-stressed condition. Compressive stress tries to make the film material expand in the plane of the film. See *Tensile stress*.

Condensation–The process whereby a vapor becomes a liquid or a solid.

Condensation energy (film formation)–The energy released upon condensing an atom or molecule from the vapor. See *Heat of vaporization*.

Conditioning, target (sputtering)–Removal of the surface contamination such as oxides and degassing of the target material, before sputter deposition begins.

Conditioning, vacuum surface (vacuum technology)–The treatment of a vacuum-surface to make the system more amenable to vacuum pumping. Treatment can include: plasma cleaning, sputter cleaning, heating, UV desorption, and/or hot-gas flushing.

Conductance (vacuum technology)–The measure of the ability of a part of a vacuum system to pass gases or vapors without a significant drop in pressure from the inlet to the outlet. The units of conductance are Torr -liters/s of flow per Torr of pressure difference.

Conductance, parallel (vacuum technology)–When there are conductance paths (C_1, C_2, …) are in parallel. The total conductance (C_{total}) is the sum of the individual conductances, i.e., $C_{total} = C_1 + C_2 + C_3 + \ldots$.

Conductance, series (vacuum technology)–When there are conductance (C_1, C_2, …) are in series. The total conductance (C_{total}) is given by $1/C_{total} = 1/C_1 + 1/C_2 + 1/C_3 + \ldots$.

Conductive heat loss–Heat flow occurring between a hot region and a colder region of a material without mass movement.

Conductivity, water (cleaning)–The measure of the ionic conductivity of water using probes spaced one centimeter part. Expressed in megohms. See *Ultrapure water, Deionized water*.

Cone formation (sputtering)–Features that develop on a surface being sputtered that are due to having a low-sputtering-yield particle on or in (inclusion) the surface. The particle shields the underlying material from being sputtered. The angle of the sides of the cone depend on the angular dependence of the sputtering yield of the bulk materials with the specific bombarding ion.

Conflat™ (CF) Flange (vacuum technology)–A demountable shear-sealing flange that uses opposing knife-edges to shear into a soft metal gasket.

Confined-vapor source (evaporation)–Evaporation source where the vapor is confined in a cavity and the substrate, such as a wire, is passed through the cavity.

Conformal target (sputtering)–A sputtering target made conformal to the shape of the substrate in order to keep a constant spacing.

Conformal anode (electroplating)–An anode made to conform to the shape of the cathode to keep the anode-to-cathode spacing constant.

Contact angle (film formation, adhesion)–The angle of contact between a fluid drop and a solid surface as measured through the liquid. In some cases the contact angle with a fluid of known surface energy can be used to measure the surface energy of the solid (dyne test). In some cases, the advancing contact angle or the receding contact angle is measured.

Contaminant (cleaning)–A material that is contaminating the surface.

Contaminant, polar (cleaning)–Contaminants that are polar materials. Example: ionic salts. See *Non-polar contaminants.*

Contaminant, non-polar (cleaning)–Contaminants that are not polar materials. Example: Oils. See *Polar contaminants.*

Contamination (PVD technology)–The materials in the vacuum system in a concentration high enough to interfere with the deposition process or to affect the film properties in an unacceptable manner.

Contamination (vacuum technology)–The materials in the vacuum system that affect the pump-down time and the ultimate pressure of the system as well as the residual contamination in the system. See *Base pressure*.

Contamination, external environment-related (contamination control)–Contamination brought-in from the external processing environment. Example: particulate contamination from dust.

Contamination, process-related (contamination control)–Contamination from the deposition process. Example: outgassing of evaporation source, volatilization of hydrocarbons from contaminated evaporation material.

Contamination, system-related (contamination control)–Contamination coming from the deposition system. Example: backstreaming from pump oils, particulates from pinhole flaking in the system.

Contamination control (cleaning)–The control of contamination and recontamination of a surface by controlling the sources of contaminants. Example: cleanrooms control the amount of particulate matter available for recontamination but do not control vapors that can recontaminate the cleaned surface.

Contractometer (electroplating)–Instrument for measuring stress in an electroplated coating.

Control samples–Samples retained after a specific portion of processing has been performed to allow comparison with material at a later stage or after being placed in service. See *Shelf samples*.

Conversion, natural (substrate)–The natural reaction of a material to form a surface layer. Example: Oxidation of aluminum or silicon after the original oxide has been removed. See *Chemical conversion*.

Converting (web coating)–The conversion of bulk metallized film into a final product such as packaging, labels, decorative products, etc. Converting can involve laminating, sealing, slitting, printing, etc.

Convertor (web coating)–A manufacturer that utilizes metallized web material to fabricate a product. See *Converting*.

Coordination number (crystallography)–The number of nearest-neighbor atoms to a point in a lattice or on a surface.

Copolymer–A mixture of two different monomers to form a polymer material that is a mixture.

Copyright (US)–The protection given to the author of a work to prevent others from reproducing the work without permission. Since March 1, 1989 all "tangible means of expression" (written words, photos, art, etc.) are automatically copyrighted. This means that permission needs to be obtained from the originator or copyright assignee for use of all or a significant part of the work. See *Patent, utility*.

Corona discharge–Electrical breakdown of the gas near a surface due to a high electric field that exceeds the dielectric strength of the gas. Usually seen at high-field points such as tips but can be found over planar electrically insulating surfaces which have been charged by an rf field. Example: St. Elmos' fire seen in nature under high electric field conditions.

Corona treatment (surface modification)–Treatment of polymer surfaces in a corona discharge in order to give the surface a higher surface energy and make it more wettable.

Corrosion–Production of an undesirable compound or surface effect by reaction with the ambient environment.

Corrosion, chemical–Corrosion by purely chemical means.

Corrosion, electrochemical–Corrosion either driven by or enhanced by the presence of an electric field.

Corrosion inhibitors–Molecular species that prevent corrosion by adsorbing on a clean surface and presenting a barrier to the corroding species. Also called *rust inhibitors*.

Corrosive fluid (cleaning)–A fluid having a pH of less than 2.0 or greater that 12.5.

Corundum (abrasive)–Aluminum oxide (Al_2O_3). See *Sapphire.*

Cosine Law, Knudsen's–The intensity of flux from a point source impinging on a flat surface normal to the direction to the point of emission is proportional to the cosine of the angle subtended by the source at the plane surface and inversely proportional to the square of the distance ($\cos\theta/r^2$).

Cost Of Ownership (COO)–Full cost of equipment including capital costs, financing costs, maintenance costs, utilities costs, operation costs, space costs, etc.

Coupling agent (adhesion)–An agent that reacts with two materials, often through different mechanisms, and allows bonding of the materials together. See *Glue layer*.

Counterflow rinse (cleaning)–Rinsing using a series of containers (tanks) having increasingly pure water. Water flows over the lip of one container into the next container having lower purity water. The surface being rinsed goes from the lower purity to the higher purity rinse tank. Also called a *cascade rinse* (preferred).

Covalent bonding–The chemical bond that is formed between two atoms which each contributes one electron. If the electrons are shared unequally it is a covalent polar bond. Also called *electron pair bond.* See *Chemical bond.*

Cracking pattern–The portion of the spectra from a mass spectrometer due to the breaking up of complex molecules by electron bombardment. Also called *fragmentation pattern.*

Crazing–A network of fine hairline cracks in a surface or coating.

Creep (contamination)–The movement of an adsorbate over a surface.

Creep (deformation)–The long-term permanent deformation of a solid under pressure.

Critical backing pressure (vacuum technology)–The foreline pressure above which a high vacuum pump will not operate efficiently.

Critical cleaning (cleaning)–Removal of contaminants from a surface to a predetermined level. Also called *precision cleaning.*

Critical point–The temperature (critical temperature) and pressure (critical pressure) at which a liquid and its vapor have the same density and other properties thereby becoming indistinguishable.

Crossection–The physical area in which an interaction can take place. Example: crossection for physical collision (sum of the radii of the particles), crossection for electron-atom ionization, crossection for charge-exchange collisions.

Crossed fields–Where the electric and magnetic fields have a vector component at an angle to one another. This situation produces a force on a charged particle moving in this region that is orthogonal to the plane of both fields. See *Drift.*

Crossover pressure (vacuum technology)–The chamber pressure at which the vacuum pumping system is switched from the rough pumping mode (roughing) to the high vacuum pumping mode.

Crosstalk (sputtering)–When material from one sputtering target is deposited on another target.

Crowding (vacuum technology)–When there is so much fixturing in the chamber that the conductance, particularly for water vapor, is reduced to the point that concentration gradients can be established in the chamber.

Crucible, evaporation–A container for holding molten material. See *Skull*.

Crucible, electrically conductive (evaporation)–A crucible of an electrically conductive material such as carbon or TiB_2 plus BN that can be heated resistively or by accelerated electrons.

Crucible, water-cooled (evaporation)–A crucible that is water cooled and where the evaporant material is heated directly by an electron beam. See *Hearth*.

Cryocondensation (vacuum technology)–Adsorption on a cold surface which may or may not be covered with an absorbate material.

Cryogenic fluid–Fluid with a boiling point below -150°C.

Cryopanel (vacuum technology)–A vapor pump that operates by cryocondensation of vapors on a large-geometrical-area cold surface at a temperature between -100°C and -150°C where the vapor pressure of water is very low. Also called a *Meissner Trap*. See *Cryopump*.

Cryopump (vacuum technology)–A capture-type pump that operates by condensation and/or adsorption on cold surfaces. Typically there are several stages of cold surfaces. Typically one of the stages will have a temperature below 120 K. See *Vacuum pump*.

Cryosorption pump (vacuum technology)–A vacuum pump that operates by cryocondensation of gases on large-adsorption-area cryogenically cooled (< -150°C) surfaces. Also called a *sorption pump.* See *Vacuum pump*.

Cryotrapping (vacuum technology)–The physical trapping of a gas in a porous material such as a zeolite or activated carbon when the surface mobility is low because of a low temperature.

Crystal structure (material)–The ordered arrangement of atoms in a solid material that is characterized by the spacing between atoms and the direction from one atom to another. The crystalline structure is comprised of repeating groups of atoms called unit cells. Also called *lattice structure*.

Crystal structure, body centered cubic (bcc)–A crystal structure where the basic building block is a cubic unit cell having atoms at each corner and one in the center of the cell.

Crystal structure, diamond–A crystal structure where each atom is at the center of a tetrahedron formed by its nearest neighbors. Example: diamond.

Crystal structure, face centered cubic (fcc)–A crystal structure where the basic building block is a cubic unit cell having atoms at each corner and one in the center of each face.

Crystal structure, hexagonal close packed (hcp)–A crystal structure where in alternate layers of atoms the atoms in one layer lie at the vertices of a series of equilateral triangles in the atomic plane, and the atoms in the layer lie directly above the center of the triangles in the atomic plane of the next layer. Example: beryllium.

Crystal structure, tetragonal–A crystal structure where the axes of the unit cell are perpendicular to each other and two of the axes are of equal length but the third is not of the same length.

Crystalline (material)–A material that has a defined crystal structure where the atoms are in specific positions and are specific distances from each other.

Crystallographic plane–One of many planes in a crystal structure that contains atoms. The areal density of the atoms and spacing between the atoms on the plane vary with direction. Also called *atomic planes*. See *d-spacing.*

Curie temperature (T_c)–Temperature above which a ferromagnetic material loses its ferromagnetism. Example: 627 K for Ni and 1043 K for Fe.

Curing, polymer–The conversion of a fluid containing monomers to a solid by polymerization. Curing may occur by reaction in a two-part system (Example: a two-part epoxy), thermal curing, electron-beam curing, ultraviolet radiation curing, etc. The curing operation can leave significant amounts of low-molecular weight material in the solid material. See *Undercuring.*

Curling, film (adhesion)–When a film separates from the substrate and curls-up due to non-isotropic stress through the thickness of the film.

Current density–Current per unit area. Example: 1 mA/cm^2 of singly-charged ions equals 1.6×10^{16} ions per second per square centimeter. See *Ampere*.

Cyanide compound (safety)–Any of a group of toxic compounds containing the CN group usually derived from the compound HCN. Concern is expressed that cyanide can be formed in plasma processing using nitrogen and a hydrocarbon.

Cyanoacrylate glue (vacuum, technology)–A class of adhesives used to bond rubber materials. Example: used to splice rubber o-rings. Also called *super glue*.

Cylindrical (hollow) *magnetron* (sputtering)–A hollow cylindrical tube often with ends flared toward the interior where a magnetic field confines the secondary electrons emitted from the inside surface to paths parallel to the axis of the tube (magnetron configuration). The flares prevent the loss of the electrons from the ends of the tube. See *Magnetron*.

Cycle time, processing–The time for one complete processing sequence including loading and unloading.

Cyclotron frequency (plasma)–Resonant adsorption of energy from an alternating electric field by electrons confined in a uniform magnetic field when the frequency of the electric field matches the oscillation frequency of the electrons in the magnetic field.

d-spacing (crystallography)–The spacing between atomic planes in a crystal lattice.

Dalton's Law of Partial Pressures (vacuum technology)–Dalton's Law of Partial Pressures states that the sum of all the partial pressures of gases and vapors in a system equals the total pressure. See *Partial pressure*.

Damage threshold (bombardment)–The energy at which radiation or bombarding particles will introduce damage to the atomic structure of a material thus changing its properties. Example: bombarding growing TiO_2 films with argon ions having an energy greater than 300 eV will increase the optical absorptivity of the deposited film material.

Damascene pattern (semiconductor metallization)–Inlay of one material into another to provide a patterned flat surface. Structure is obtained in semiconductor processing when a material is deposited in vias and trenches on a surface then the high areas are polished back to the original surface. See *ChemoMechanical Polishing (CMP)*.

Dangling bonds–An unsatisfied chemical bond that is available to react with atoms or molecules. See *Sensitization, surface*.

Dark space, cathode (plasma)–The darker region of a plasma near the cathode surface where most of the potential drop in a DC diode discharge occurs. Region where electrons are being accelerated away from the cathode. Also called the *cathode sheath*.

Dark space shield (plasma)–A grounded surface that is placed at less than a dark space width from the cathode in order to prevent establishing a discharge in the region between the two surfaces. Also called the *ground shield*. See *Paschen curve*.

DC glow discharge (plasma)–The plasma discharge established between two electrodes in a low-pressure gas and in which most of the potential drop is near the cathode surface and a plasma region (positive glow) where there is little potential drop that can extend for an appreciable distance.

De-excitation (plasma)–The return of an electron in an excited state to a lower energy level accompanied by the release of optical radiation. Also called *relaxation*.

De-wetting growth (film formation)–When the nuclei tend to grow normal to the surface rather than laterally over the surface. See *Wetting growth*.

De-adhesion–The loss of adhesion. See *Adhesion*.

Debug–To eliminate the initial problems in an electronic circuit or a software program.

Deburring–The removal of burrs formed during deformation or cutting operations.

Decarburizing–The loss of carbon from a carbon-containing compound or alloy. The loss may be due to diffusion, vaporization or chemical reaction.

Decomposition Reaction (CVD)–Deposition by decomposition of a chemical vapor precursor species. Example: Si from SiH_4.

Decorative coating–A coating whose function is to be decorative so that the properties of the coating of interest are primarily reflectivity, color, color distribution and texture. Example: Aurora Borealis coating.

Decorative/wear resistant coating–A coating which has both the requirement of a decorative coating but also must withstand wear, such as abrasive cleaning. Example: decorative coating on a plumbing fixture or door hardware. Also called *decorative/functional coating*.

Deep ultraviolet (DUV)–Short wavelength ultraviolet radiation.

Defects, film (film formation)–Any irregular feature of the film crystallinity, microstructure or morphology that can affect the film properties. Example: pinholes, voids, column boundaries.

Defects, lattice (crystallography)–Any departure from crystalline order such as vacancies, substitutional atoms, interstitial atoms, dislocations, grain boundaries, etc.

Defects, surface (substrate)–Any feature on the surface that disrupts the regularity and that might influence film growth, film properties or film adhesion. Example: scratches, microcracks, electronic charge sites.

Deflected electron beam (evaporation)–An e-beam evaporation source where the electron beam is deflected out of the line of sight of the electron emitter to impinge on the surface of the charge. The e-beam can be focused and rastered over the surface of the charge during heating.

Deflocculants (cleaning)–Chemicals that are added to solutions to help maintain the dispersion of contaminants in the cleaning medium.

Degas (fluids)–Removal of gases and vapors from a liquid or solid, usually by heating or reduction in pressure above the surface. Also called *exosolution*. See *Outgas*.

Degassing rate–The rate at which gases or vapors leave a surface. Measured in Torr-liters/sec-cm^2 or grams/sec-cm^2. See *Outgassing rate*.

Degreaser, vapor (cleaning)–A cleaning system where the surface to be cleaned is placed in the hot vapor of the cleaning solvent. The vapor condenses on the surface dissolving the contaminant and flows off into the sump. When the part reaches the temperature of the vapor, condensation stops and the part is removed. In the old-style degreaser, that was open to the atmosphere, there was a spray wand that allowed spraying the part while in the vapor. See *Degreaser, vapor, low-emission; Drying, vapor*.

Degreaser, vapor, low-emission (cleaning)–A degreaser where the cleaning solvent is contained in an enclosed cleaning chamber and then pumped away before the cleaning chamber is opened. The vapors are condensed and returned to the cleaning liquid sump.

Deionized (DI) water (cleaning)–Water in which most of the ions, which have a potential for reaction with cleaning materials and/or leaving a residue, have been removed. Often used (erroneously) synonymously with ultrapure water. For deionized water the electrical conductivity can be as low as 18.2 megohm-cm at room temperature. See *Conductivity, Ultrapure water*.

Deliquescent (vacuum technology)–Material that reversibly absorbs and desorbs water from the air and tends to liquefy. Example: NaCl (common table salt).

Demister (vacuum technology)–A baffle on the exhaust of an oil-sealed mechanical pump used to condense oil vapors to reduce the loss of oil from the pump.

Denatured alcohol (cleaning)–Ethyl (grain) alcohol that has be rendered unfit to drink by the addition of another material (denaturant).

Density–The mass per unit volume (g/cm^3) of a material. See *Specific gravity*.

Density gradient column (characterization)–A liquid column in which the density of the liquid is varied by having a temperature gradient. An object immersed in the liquid will float at a level where its density matches that of the fluid.

Deposition rate–Mass or thickness of material deposited per unit time. Measured in micrograms per cm^2 per sec, nanometers per second or Angstroms per second.

Deposition system (PVD technology)–A vacuum system used for physical vapor deposition processing.

Deposition system, cluster-tool (semiconductor processing)–A load-lock vacuum system that has random access to several processing modules from the loading chamber.

Deposition system, direct-load–A system where the processing chamber is opened to the ambient each time the fixture is placed into or removed from the chamber. Also called a *batch system*.

Deposition system, dual-chamber–A chamber which has two separate sections separated by a low conductance path. The sections may be independently pumped or there may be two different gas pressures in the sections. This allows high gas load operations, such as unrolling a web, to be performed in a section separate from the film deposition section.

Deposition system, load-lock–A system which has a chamber intermediate between the ambient and the deposition chamber that allows the substrate to be outgassed, heated, etc., before being placed in the deposition chamber. The substrates are passed from the load-lock chamber into the deposition chamber through an isolation valve using transfer-tooling. In the rotary load-lock the substrate passes through several chambers before returning to the insertion/removal chamber.

Deposition system, in-line–A series of sequential vacuum modules in a line beginning and ending with load-lock chambers that allows the substrate to enter one end and exit the other end without reversing direction.

Deposition system, web coater–Specialized direct-load deposition system used to coat web material which is often on very large, heavy rolls. Often a dual-chamber system. Also called a *roll coater.*

Depth profiling (characterization)–The determination of the elemental composition as a function of distance from the surface. The analysis may be destructive (e.g., sputter profiling in Auger Electron Spectroscopy) or non-destructive (e.g., Rutherford Backscattering Spectrometry).

Descale (cleaning)–The chemical or electrochemical removal of thick oxide layers (scale) from a surface.

Desiccant (cleaning)–A chemical that has a great affinity for water and will reduce the relative humidity in its surroundings to a very low value.

Design rule (semiconductor processing)–Spacing between interconnect metallization lines (e.g., 0.35 micron design rule).

Desize (cleaning)–Removing the sizing (lubricant) from a cloth by washing in hot water.

Desorption–To remove gases and vapors from a material, usually by heating but also by electron impact, ion impact, etc. See *Outgas*.

Desorption energy–The amount of energy necessary to cause an atom or molecule to vaporize from a surface or from the bulk of the material. See *Thermal desorption spectrum*.

Detergent (cleaning)–A substance that reduces the surface tension of water, concentrates at the water-oil interface and takes oils into suspension (emulsifies them). Detergents can be of several types: anionic detergents, cationic detergents or non-ionic detergents.

Detonation gun deposition (thermal spray)–A thermal spray process in which the particles are melted in an explosion front and propelled to a high velocity in a "gun barrel."

Devitrification–Crystallization of a glassy material.

Dew point, water–The temperature at which the vapor pressure of water reaches saturation and the vapor begins to condense into a fluid. See *Humidity*.

Dewar vessel (vacuum technology)–A vacuum-insulated container commonly used to contain liquefied gases.

Dewetting growth (film formation)–When nuclei on a surface grow by atoms avoiding the surface and the nuclei grow normal to the surface. Example: gold on carbon. See *Wetting growth*.

Diamond (abrasive)–The crystalline form of carbon that is very hard. Commonly available in abrasive particle sizes down to 0.25 micron.

Diamond-like carbon (DLC)–An amorphous carbon material with mostly sp^3 bonding that exhibits many of the desirable properties of diamond but does not have the crystal structure of diamond.

Diamond point turning (substrate)–Machining a metal using a light-cut with a very sharp, wear-resistant point on a diamond tool thus obtaining a very smooth, mirror-like as-machined surface.

Diaphragm pump–A gas or fluid pump that operates by the periodic expansion and reduction of a chamber volume by the action of a piston-actuated flexible (usually polymeric) diaphragm. In vacuum applications the diaphragm pump can be used at pressures down to 10 Torr at the inlet with an exhaust to atmospheric pressure.

Diatomaceous earth (cleaning)–Soft material (88% silica, balance calcium carbonate) composed of the skeletons of small prehistoric aquatic plants. Used as a mild abrasive and as a filtration material. When the calcium carbonate is removed by acid washing, the material is used as a fine silica abrasive.

Dichroic coating–An optical coating that reflects certain wavelengths and allows others to pass through. Example: heat mirror, sunglass coatings. See *Ophthalmic coatings, Band-pass coatings*.

Die (semiconductor)–The conductor circuit pattern on the surface of a chip which is connected to a printed circuit board or chip carrier by wires (to a lead-frame) or solder bumps (flip-chip bonding).

Dielectric constant (material)–The ratio of the capacitance of a capacitor constructed using the dielectric material as the insulator between the electrodes, to a capacitor using vacuum between the two electrodes.

Dielectric material–A material which is an electrical insulator.

Dielectric strength–The voltage gradient that can be tolerated by a material without an electrical breakdown (arc) through the material.

Differentially pumped (vacuum technology)–A system or component in which one region is pumped differently from another. This may be done using different pumps or by different pumping manifolds. Example: differentially pumped, dual o-ring sealed, mechanical motion feedthrough where the space between o-rings on the shaft is pumped.

Diffuse reflection–Optical reflection in many directions. Diffuse reflection is due to surface roughness on the order of the wavelength of the light or greater. Also called *non-spectral reflection*. See *Scatterometry, Spectral reflection*.

Diffusion–The movement of one atomic, ionic or molecular species through another due to a concentration gradient or an electric field gradient.

Diffusion-type interface (film formation)–When the interfacial material (interphase material) that has been formed during the deposition of A onto B along with subsequent diffusion, consists of an alloy of A and B with a gradation in composition. See *Interface, Kirkendall porosity, Interphase material*.

Diffusivity–The rate of diffusion across an area. Also called the *diffusion coefficient*.

Diffusion pump (DP) (vacuum technology)–A compression-type vacuum pump that operates by the collision of heavy vapor molecules with the gas molecules to be pumped, giving the gas molecules a preferential velocity toward the high pressure stages of the pump. See *Vacuum pump*.

Diluent gas (CVD)–A gas that does not enter into the deposition process but is used to control the partial pressure of the precursor gas at a given total gas pressure. Also called *carrier gas.*

Diluent gas (vacuum technology)–Dry gas used to dilute a vapor-containing gas to the point that the vapor will not condense during compression in a mechanical pump. See *Ballast valve*.

Dimers–A vapor species consisting of two molecules.

Dioctyl phthalate (DOP) (contamination control)–A chemical used to generate the white fog that is used to test HEPA filters.

Dip coating–Where the part is dipped into a fluid and the fluid is allowed to drain off the part. The viscosity of the fluid determines the coating thickness.

Disappearing anode effect (sputtering)–In reactive deposition of electrically insulating films, the surfaces in the deposition chamber become covered with an insulating film and the electron flow to the grounded surface (anode) must change position as the surfaces become coated.

Discharge pressure (vacuum technology)–The pressure at the outlet of the high pressure stage of a vacuum pump. Also called *exhaust pressure*. See *Foreline pressure*.

Dislocation, lattice (crystallography)–A line of displacement of atoms in a lattice. Often formed during mechanical stress to relieve some of the stress.

Dispersion (cleaning)–To break big particles into small particles that can be suspended in water. Alkaline silicates and alkaline phosphates are used as dispersion agents in some cleaning formulations.

Dispersion strengthening–When a small amount of a second phase in the form of small particles is dispersed in a matrix and strengthens the material. The particles may be mixed with the material in the melt or be formed by reaction and precipitation after the solid has been formed.

Displacement plating–When an ion in solution that has a less negative potential than the atom of the solid, spontaneously displaces the atom of the solid and deposits it on the solid. Example: Au (+1.50 volts) plating onto Cu (+0.52 volts), Pb (-0.126 volts) or Sn (-0.136 volts) (from solder) plating on Al (-1.67 volts). Also called *immersion plating.* See *Electrochemical series*.

Disproportionation reactions (CVD)–A reaction where the oxidation number of the element both increases and decreases through the process. Process can be use to purify materials.

Dissociation (plasma chemistry)–Separation of a molecule into two or more fragments due to collision (example: electron–molecule) or the adsorption of energy (example: photodissociation). See *Fragmentation.*

Dissociative attachment (ionization, plasma chemistry)–When a molecule combines with an electron, loses a fragment and becomes a negative ion. Example: $SF_6 + e^- \varnothing SF_5^- + F$ (SF_6 is a good electron scavenger in a plasma.).

Documentation (manufacturing)–The documentation that is maintained in order to know what was done during the processing and the status of the processing equipment. This enables reproducible processing to be performed.

Documentation, Log–A dated document detailing who, when and what was done. See *Log, calibration, Log, maintenance, Log, run time*.

Documentation, Manufacturing Processing Instruction (MPI)–Detailed instructions for the performance of each operation and the use of specific equipment, based on the specification, that apply to each stage of the process flow. MPIs are developed based on the specifications.

Documentation, Process Flow Diagram (PFD)–A diagram showing each successive stage in the processing sequence including storage, handling and inspection. A PFD is useful in determining that there are MPIs that cover all stages of the processing.

Documentation, Specifications (Specs)–The formal document which contains the "recipe" for a process and which defines the materials to be used, how the process is to be performed, the parameter windows and other important information related to safety, etc. Information on all critical aspects on the process flow sheet should be covered by specifications.

Documentation, Travelers–Archival document that accompanies each batch of substrates detailing when the batch was processed and the specifications and MPIs used for processing. The traveler also includes the process sheet which details the process parameters of the deposition run. Also called a *run-card* in semiconductor processing.

Dog-boning (electroplating)–When the deposit builds up at a faster rate at high field regions, such as at corners, compared to a flat region.

Donor, electrical–An impurity (dopant) that increases the number of free electrons in the material. See *Acceptor*.

Dopant (semiconductor)–A chemical element added in small amounts to a semiconductor material to establish its conductivity type and resistivity. Example: phosphorus, arsenic and boron. See *Donor, Acceptor.*

Dopant (glass)–A chemical element that is added to give color to a glass.

Dose (ion bombardment)–The total number of bombarding particles per unit area.

Double bond–A type of chemical bonding where two pairs of electrons are shared equally between two atoms. Symbolized by (=). Example: C=O.

Downtime–The amount of time that a pump or system is not operational due to failure or maintenance requirements. See *Uptime*.

Downstream region (plasma technology)–See *Afterglow region.*

Drag finishing (substrate)–Polishing a surface by pulling individual parts through an abrasive media. This prevents part-to-part contact that can cause damage.

Drag pump, molecular (vacuum technology)–A vacuum pump that imparts a preferential motion to a gas molecule by the friction between the gas and a high velocity surface. See *Vacuum pump*.

Drag-out (cleaning, electroplating)–The transfer of fluid from one tank to the next by virtue of the liquid material retained on the surface. Drag-out often necessitates a rinse step between the two tanks to prevent contamination of the second tank.

Drift, **E X B**–The motion of an electron in a direction normal to the plane defined by the electric and magnetic field vectors.

Drift, gauge (vacuum technology)–The change of calibration of a sensor with time or use.

Dry (cleaning)–Removal of water from a surface after processing, hopefully without leaving a residue. See *Water spot.*

Dry, blow-off–Removal of water by blowing it off a surface with a high velocity gas stream. See *Air knife*.

Dry, displacement–Removal of water by taking it into solution with another fluid (drying agent) such as anhydrous alcohol, that has a rapid drying rate when pure.

Dry, hot gas–Using a hot dry gas to dry a surface.

Dry, spin–Drying by spinning the surface at a high velocity and slinging the water off the edges. See *Spin coat*.

Dry, vapor (cleaning)–A cleaning system where the surface to be dried is placed in the hot vapor of the drying agent. The vapor condenses on the surface dissolving and displacing the water and flowing off into the sump. When the part reaches the temperature of the vapor, condensation stops and the hot part is removed where it dries rapidly. See *Drying, vapor, low-emission; Degreasing, vapor*.

Drying, vapor, low-emission (cleaning)–A drying system where the drying agent is contained in the drying chamber and then pumped away before the drying chamber is opened. The vapors are condensed and returned to the drying agent sump.

Dry gas–A gas with a very low dew point for water. Example: dry air with a dew point of -100°C (used to thermally oxidize electropolished stainless steel tubing), dry hydrogen with a dew point of -70°C (commercial grade dry hydrogen).

Dry process–A process that uses no fluids. Often desirable in context of waste disposal.

Dry pump (vacuum technology)–Vacuum pump that uses no (or little) oil, that can become a source for contamination. See *Vacuum pump*.

Dry pumping (contamination control)–Vacuum pumping using one or more dry pumps to avoid the possibility of oil contamination. Example: a turobopump with a molecular drag stage backed by a diaphragm pump.

Dual-containment piping–A configuration where an exterior pipe surrounds the supply pipe that carries a high-purity or hazardous gas or liquid. The outer volume can be evacuated and monitored for safety.

Ductile fracture–Fracture that is accompanied by appreciable plastic deformation.

Ductile material–A material that undergoes appreciable plastic deformation before failure. See *Brittle material*.

Ductility–The ability of a material to plastically deform under applied stress. See *Elongation, Elasticity*.

Dummying a bath (electroplating)–Removing tramp elements from the electrolyte by plating them out before the product is coated.

Duplex steel (substrate)–A simple alloy of iron and carbon perhaps with a little Si, Ni or Mn. The alloy has high ductility and easy formability, used in stamping parts such as auto fenders. Also called *dual-phase steel*.

Dust balls (cleaning)–Balls of lint that accumulate lint by rolling around on the floor in air currents. Also called *dust bunnies*.

Dusters (cleaning)–Soft mop-like dusters, often made of electret material, used to collect dust and not generate particulates.

Duty cycle–The ratio of the working time to the total time of a piece of equipment.

Dwell (cleaning)–The time the part remains in a specific cleaning stage. Example: in the vapor of a vapor degreaser. See *Soak*.

Dyne test (surface)–Determining the surface energy of a polymer by applying fluids with known surface energies to the surface and monitoring the contact angle or by marking with materials (e.g., dyne-test marker pens) having progressive (30-60 dyne/cm) surface energies.

E-beam evaporation (PVD technology)–Evaporation using a focused high-energy low-current electron beam as the means of directly heating the material to be evaporated.

Effusion cell–A thermal vaporization source which emits vapor through an orifice from a cavity where the vapor pressure is carefully controlled by controlling the temperature. Example: used in MBE processing. Also called a *Knudsen cell*.

Elastomer–Material that is elastic or rubber-like, i.e., under stress it can deform to a large extent, exert a restoring force and then return to its original shape when the deforming force is removed.

Elastomer seal (vacuum technology)–A deformation seal that is made from an elastomer such as Viton™, butyl-rubber or neoprene.

Electret (cleaning)–A polymer material that has a permanent electric polarization charge. Usually formed by deformation of a polymer in an electric field.

Electrical resistance–The electrical resistance (R) of a conductor is given by: $R = \rho L/A$ where (ρ is the bulk resistivity in ohm-cm, L is the length of the conductor in cm, and A is the crossectional area of the conductor in cm^2. See *Sheet resistivity.*

Electrochemical polishing–Smoothing a surface by a combination of chemical polishing (selective chemical dissolution of high points) and electropolishing (selective off-plating of high points).

Electrochemical series–The relationship of materials as to their electrode potential (tendency to lose electrons as related to a platinum/hydrogen electrode i.e., electrode potential). Also called the *electromotive series*.

Electrochromic film (optics)–A thin film structure that changes optical density under the influence of an applied electric field.

Electrode–An electrically conductive surface that is active in carrying and electric current. See *Cathode, Anode*.

Electrode potential–The voltage generated when a material is immersed in an electrolyte and usually referred to a standard platinum/hydrogen electrode used as the zero potential. See *Electrochemical series*.

Electrocleaning (cleaning)–Removal of a material from substrate which is made the electrode (cathode or anode) of an electrolysis cell.

Electrocoating–The deposition of particles (paint, glass, etc.) from an electrolyte under an applied voltage. The deposition can either be on the cathode (cathodic electrocoating) or the anode (anodic electrocoating). Also called *electrophoretic deposition.*

Electrodeposition–The deposition of ions from a solution on the cathode of an electrolysis cell. Generally the ions lost from the solution are replenished by dissolution of the anode. Also called *electroplating.*

Electroetching (cleaning)–Electrolytic removal of material from an anodic surface without the presence of a passivating surface layer. See also *Electropolish.*

Electroforming (electroplating)–The generation of a free-standing structure by electrodeposition on a shaped mandrel and then removing the mandrel. See *Vapor forming*.

Electrographic printing (characterization)–A method of locating pinholes in a film by reacting the exposed substrate with a wet chemical in an applied electric field to form a colored corrosion product that can be visually observed.

Electrography–Forming an image by the attraction of electrically charged "toner" to a selenium (or other photosensitive material)-coated drum which has been charged by exposure to an optical image, transferring the toner to paper and then fusing the toner to the paper with heat. Also called *xerography* and *electrophotography*.

Electroless plating–Deposition of a coating from a solution by use of a reducing agent in the solution rather than an external-applied electrical potential. Example: electroless Ni, Cu.

Electrolysis–A method by which chemical reactions are carried out by passing an electrical current through an electrolyte.

Electrolyte–A solution or gel containing a chemical compound which will conduct electricity by virtue of dissociation of the chemical compound into ions that are mobile in the media.

Electrolytic anodization (surface modification)–Oxidation of the surface of a material at the anode of an electrolysis cell. See *Anodization*.

Electrolytic conversion–The production of a compound layer on the surface of an electrode in an electrolysis cell. Example: anodization.

Electromigration (semiconductor)–The movement of atoms in a metallic conductor stripe under high current conditions ($>10^6$ A/cm^2 in aluminum).

Electromotive series–See *Electrochemical series*.

Electron–Elementary particle having a negative charge and a mass of approximately 1/1840 that of a hydrogen atom.

Electron beam (e-beam) (evaporation)–Heating and evaporation of a material by an electron beam. The electron beam generally has a low-current of high-energy electrons and is directed to the surface of the material to be evaporated and may be rastered over the surface during heating. Electron beam of low-energy and high-current can be used to evaporate material but the term e-beam is generally applied to a beam using high-energy electrons.

Electron cyclotron resonance (ECR) plasma source (plasma technology)–A plasma source where the microwave energy, which has a resonant frequency of the electron in a magnetic field, is injected into the plasma-generating region through a dielectric window. See *Plasma source*.

Electron impact excitation (plasma chemistry)–Excitation of an atom or molecule by electron impact. See *Excitation*.

Electron impact ionization (plasma chemistry)–Ionization of an atom or molecule by the impact of an electron causing the loss of an electron. See *Ionization.*

Electron impact fragmentation (plasma chemistry)–Fragmentation of a molecule by electron impact.

Electron Spectroscopy for Chemical Analysis (ESCA) (characterization)–A surface analytical technique where the probing species are X-rays and the detected species are photoelectrons. The technique allows identification of species on the surface and the chemical binding energy. Also called *X-ray Photoelectron Spectroscopy* (XPS).

Electron temperature (plasma)–A measure of the average kinetic energy of electrons in a plasma.

Electron volt (eV)–The amount of kinetic energy imparted to a singly charged particle when accelerated through a potential of one volt. Equal to 1.602 x 10^{-19} joules.

Elecronegativity–The relative propensity for an atom to lose or gain an electron as given by the electromotive series.

Electronic filter (cleaning)–An air filter that ionizes particulates in a high electric field and the charged particles are then attracted to electrically grounded surfaces. See *Electrostatic filter, Mechanical filter*.

Electronic grade material–A purity grade for materials that are to be used in electron devices such as electron tubes.

Electro-optical property (film)–A property of a film such as optical transmission or color, that is affected by electric fields.

Electrophoresis–The migration of large electrically charged solid particles or liquid droplets in a fluid medium under the influence of an electric field. Also called *cataphoresis*.

Electrophoretic deposition–Deposition of larger-than-ion charged particles from a solution by electrophoresis. Particles can be of glass, polymer, a liquid, etc.

Electroplating–Deposition of ions of a material from an electrolyte on the cathode of an electrolysis cell. Generally the ions being removed are replenished by dissolution of an anode of the material being deposited. Also called *electrodeposition*.

Electropolishing–Electrolytic removal of material from the high points on an anodic surface with passivation (usually by phosphates) of the smoothed areas. See *Electroetching*.

Electrostatic charge–The potential on an electrically isolated part or surface.

Electrostatic filter (cleaning)–A filter that attracts charged particles by virtue of a permanent electrostatic charge on the filter material. See *Electret, Electronic filter, Mechanical filter*.

Electrostatic spraying–Coating using a spray of liquid or solid particles having an electric charge so that they can be directed to the substrate by an electric field. Example: powder coating.

Ellipsometry–The technique for determining the optical constants or thickness of a film by determining the change in phase and amplitude of the electrical field vector of light reflected from the surface.

Embrittlement–Loss of ductility due to the incorporation of a foreign species which changes the chemical bonding. Example: hydrogen and helium embrittlement of steel, mercury embrittlement of aluminum.

Emery–A natural abrasive material consisting of 55-75% aluminum oxide and the rest being iron oxide and other impurities.

Electromagnetic Interference (EMI) shielding–Thick deposits of metal to prevent electromagnetic radiation from penetrating into a container and affecting electronic components.

Emery (abrasive)–An abrasive of impure corundum (Al_2O_3).

Emission spectrum, optical (plasma)–The de-excitation spectrum (color), of atoms and molecules in a plasma. The intensity of the peaks in the spectrum will change with changes in the plasma parameters.

Emulsification (cleaning)–To establish a stable suspension of particles in a fluid by coating them with a surfactant that prevents them from combining into large masses.

Emulsion cleaner (cleaning)–A cleaning solution consisting of an organic solvent emulsion suspended in a water base.

Enabling technology (manufacturing)–Euphamism for the processes and equipment that work.

Enameling–Fusion coating where the coating consists of a glassy matrix that bonds to the substrate surface. See *Fusion coating*.

Enclosed system (cleaning)–Cleaning, rinsing and drying systems where the liquids are contained and vapors are condensed and recycled. This reduces pollution generation. Example: vapor cleaners, spray cleaners and vapor dryers. See *Closed loop system*.

End-Hall plasma source (plasma technology)–A plasma source that uses a thermoelectron emitter and a magnetic field to confine the electrons so as to impinge on gas molecules exiting an orifice. See *Plasma source*.

Endothermic process–A process that adsorbs energy. Example: endothermic chemical reaction; endothermic phase change.

Endpoint, etching (plasma, semiconductor processing)–The point at which a film has been completely removed as determined by optical emission from the plasma.

Energy–The capacity for doing work.

Energy, kinetic–The energy available due to motion. Example: high speed ion.

Energy, potential–The energy available due to position or condition. Example: excited state of an atom.

Engineering notebook–A notebook containing dated entries detailing experiments performed, results obtained and ideas conceived. For patentable ideas and findings the entries should be read and dated by a non-involved person. Also called a *laboratory notebook*.

Enthalpy–Heat (energy) content of a system. Example: a high enthalpy plasma is one that has a high density of energetic particles such as an atmospheric electric arc.

Entropy–A measure of the disorder in a system.

Epitaxial growth (film formation)–Growth of one crystal on another such that the growth of the deposited crystal is determined by the crystalline orientation of the underlying surface.

Epitaxy–Oriented overgrowth of an atomistically deposited film. See *Epitaxial growth, Homoepitaxy, Heteroepitaxy*.

Epitaxy, Heteroepitaxy–Oriented overgrowth on a substrate of a different material or the same material with a different crystalline structure. Example: silicon on sapphire.

Epitaxy, Homoepitaxy–Oriented overgrowth on a substrate of the same material. Example: silicon on doped silicon.

Equilibrium vapor pressure–The pressure above a surface when there are as many atoms leaving the surface as are returning to the surface (isothermal closed container). See *Saturation vapor pressure*.

Equivalent weight–The weight of an element or molecule that will combine chemically with 8 grams of oxygen or 1.008 grams of hydrogen. Also called *combining weight*. Example: gram equivalent weight.

Ergonomic (furniture)–Designed for comfort and support for a type of job. To reduce stress and strain on the operator.

Escape depth (characterization)–The depth from which the species to be detected (electron, X-ray, ion) can escape after being created. Example: the low-energy auger electron created in AES can escape from only a few angstroms under the surface of a metal.

Etch rate (characterization)–The amount of material (mass or thickness) removed per unit time. Often used as a comparative test.

Etch tunnel (barrel etcher)–A tube-shaped grid for shielding the etch region from the rf which sustains the glow discharge in a barrel etcher. The etch tunnel makes the etch region into an afterglow region. See *Plasma etcher, Afterglow region*.

Etchant–The chemical used for etching.

Etching–The removal of material by chemical reaction to form a soluble or volatile compound.

Etching, cleaning by–Removing surface (often substrate material) material by chemical etching. Removal of the surface material also removes the contamination. See *Gross cleaning*.

Etching, plasma–Etching in a plasma.

Etching, sputter–Etching a surface by sputtering. Sputter etching is used to clean a surface and to also reveal different crystallographic orientations of the grain structure in the surface.

Etching, vapor–Etching in a chemical vapor.

Etching, wet chemical–Etching in a chemical fluid.

Ethanol (cleaning)–An alcohol that is completely miscible with water and is often used to wipe-down vacuum surfaces. See *Anhydrous alcohol*.

Ethyl alcohol (cleaning)–A non-toxic alcohol derived from grain. Also called *grain alcohol*. See *Denatured alcohol*.

Ethylene diamine tetraacetic acid (EDTA) (cleaning)–A cheleating agent.

Evaporant (PVD technology)–The material to be evaporated.

Evaporation–Vaporization from a liquid surface. See *Sublimation*.

Evaporation-to-completetion (PVD technology)–Complete vaporization of the charge of evaporant. A common method of obtaining reproducible film thickness from run-to-run if the geometry of the system and other conditions remain constant.

Evaporation rate, free surface–The amount of material leaving the surface per unit of time when there are no collisions above the surface to cause backscattering of the material to the surface. See *Langmuir Equation.*

Evaporation source (PVD technology)–The source used to evaporate a material.

Evaporation source, e-beam, focused–Evaporation using a focused high-energy low-current electron beam as the means of heating the surface of the material directly.

Evaporation source, e-beam, unfocused–Evaporation using an unfocused low-energy high-current electron beam as the means of heating the material directly or by heating the crucible containing the material.

Evaporation source, baffle–An evaporation source in which the vapor must collide with several hot surfaces before it can leave the source. Used to evaporate materials such as selenium and silicon monoxide which vaporize as clusters of atoms or molecules.

Evaporation source, boat–Evaporation from a resistively heated surface in the shape of a boat or canoe.

Evaporation source, coil–A thermal evaporation source in the form of a coil, usually of stranded wire, that is wetted by the molten material and allows deposition in all directions.

Evaporation source, confined vapor–A thermal evaporation source where the vapor is confined in a cavity and the substrate, such as a wire, is passed through the cavity.

Evaporation source, crucible–A container for holding a large amount of molten material. The crucible may be of a number of shapes such as a symmetrical pot or a high-capacity elongated trough (Hog-trough crucible).

Evaporation source, feeding–An evaporation source in which the evaporant material is replenished either during the deposition process of after the deposition process.

Evaporative cooling (vacuum technology)–The cooling of a liquid due to rapid evaporation. In the limit the cooling can actually freeze water in the vacuum system.

Evaporative rate analysis (ERA) (cleaning)–ERA measures the evaporation rate of a radioactive-tagged material that is absorbed in the contaminants on the surface.

Excimer laser–A laser based on a noble gas such as helium or neon where the radiation is from a transition between an excited state and a rapidly dissociating ground state.

Excitation, atomic–The elevation of outer-shell electrons of an atom to a higher energy state. De-excitation gives rise to optical radiation. See *De-excitation, Optical radiation, Metastable state*.

Exempt solvents (cleaning)–Solvents not subject to pollution regulations. Example: Biodegradable soaps.

Exhaust baffle (vacuum technology)–See *Demister*.

Exhaust pressure (vacuum technology)–The pressure at the exhaust port of a vacuum pump or in the plumbing from the pumping system to the ambient environment.

Exhaust system (vacuum technology)–The plumbing system that removes gases and vapors from the work area and is located downstream from the last vacuum pump. This portion of the vacuum system can contain scrubbers to remove undesirable gases and vapors. The exhaust system should not present excessive backpressure on the vacuum pumping system, particularly during start-up. See *Scrubbers, Backpressure*.

Exhausted cleaner–A cleaning solution in which the cleaning agents have been depleted to the point that the cleaner is deemed ineffective.

Exoemission (adhesion)–The emission of electrons during fracture. Also called *fractoemission*.

Exosolution (fluid)–Removal of gases from a fluid generally by reduction of pressure or by heating. Also called *degassing.*

Exothermic–A process that releases energy. Example: exothermic chemical reaction, exothermic phase change. See *Endothermic process*.

Exploding wire, evaporation (film deposition)–The heating and vaporization of a wire by the sudden discharge of an electrical current through the wire and the deposition of the vapor and molten globules thus formed. See *Flash evaporation*.

External cleaning (cleaning)–Cleaning external to the deposition system.

External processing environment (PVD technology)–The processing environment external to the deposition system in which processes such as cleaning, racking and unracking take place.

Extinction coefficient (optical)–The optical adsorption per unit path length in a material. Also called *optical adsorptivity*.

Extractables (cleaning)–Materials that can be extracted from a solid by solvents that it may come into contact with. Example: extracting phthalates from vinyl gloves by alcohol.

Fab (semiconductor processing)–A production facility, usually for one specific product.

Face masks (contamination control)–Face coverings to prevent contamination from fluids from the mouth or nose, or particulates from the face or facial hair.

Face mask (safety)–Face coverings to prevent chemicals from coming into contact with the face.

Fail-safe design (vacuum technology)–A design such that the system will assume a safe and non-contaminating configuration if there is a mechanical, electrical, or coolant failure. See *What-if game*.

Failure analysis (adhesion)–The analysis of the failed interface and other contributing factors to try to determine the cause of the failure.

Fahrenheit temperature scale–A temperature scale based on the freezing point of water being 32ºF and the boiling point of water being 212ºF under standard pressure conditions. See *Temperature scale*.

Faraday's Law of Electrolysis–Faraday's Law of Electrolysis states that the amount of material dissolved or deposited in an electrolysis cell is proportional to the total charge passed through the cell.

Fatigue–Reduction of some property of a material after some period of stress.

Fatigue, chemical–Fatigue after exposure to a chemical environment. Example: reduction in strength due to stress corrosion.

Fatigue, mechanical–Fatigue under mechanical motion, deformation, etc. Example: work hardening reducing the ductility of a metal.

Fatigue, static–Fatigue due a continuously applied stress with no motion. Example: static fatigue failure in glass.

Feedback (process)–The control of the output of a process by the return of information about the output to the input.

Feeding source (evaporation)–An evaporation source in which the evaporant material is replenished either during the deposition process or after the deposition process. See *Evaporation source, Flash evaporation*.

Feeding source, pellet–A mechanism to feed individual pellets into a molten pool to replenish the charge or onto a hot surface for flash evaporation.

Feeding source, powder–A mechanism to feed powder into a molten pool to replenish the charge or onto a hot surface for flash evaporation.

Feeding source, rod-feed–A focused e-beam source where the surface of the end of a rod is being heated and the molten material is contained in a cavity of the rod material. As the material is vaporized the rod is moved so as to keep the molten material in the same position with respect to the e-beam.

Feeding source, tape feed–An evaporation source where the melt material is continually or periodically renewed by a tape being fed into the molten material. Generally a tape is easier to feed than a wire.

Feeding source, wire feed–An evaporation source where the melt material is continually or periodically renewed by a wire being fed into the molten material.

Feedthrough (vacuum technology)–A device for transmitting electrical, optical or mechanical signals or fluids through the wall of a vacuum chamber. The feedthrough is generally mounted on a flange. See *Flange*.

Feedthrough, electrical–A feedthrough that allows passage of electrical signals into the deposition chamber.

Feedthrough, fluid–A feedthrough that allows passage of fluids into the deposition chamber. The fluid may be hot or cold even to cryogenic temperatures.

Feedthrough, magnetic–A feedthrough that allows passage of magnetic flux into the deposition chamber.

Feedthrough, mechanical–A feedthrough that allows passage of mechanical motion into the deposition chamber. The vacuum sealing may be by differentially pumped o-rings, ferrofluidic seals, rotary magnetic drive through a solid metal wall or by a wobble motion using a bellows to give a rotary motion in the chamber.

Feedthrough, optical–A feedthrough that allows passage of optical signals into or out of the deposition chamber. When used to observe the processing it is called a *window.*

Ferric oxide (Fe_2O_3)–A polishing compound. Also called *jeweler's rouge* or *red ochre*. See *Cerium oxide (CeO_2)*.

Ferromagnetic material–Material in which the electron spins can be preferentially oriented to produce a permanent magnetic moment even when there is no externally applied magnetic field.

Field-free region (plasma)–A region in which there is no electric field. Usually generated by having the region surrounded by an electrical conductor (soild or as a grid).

Field emission, electron–Emission of electrons under a high electric field, usually from a point.

Field emission, ion–Creation of gaseous ions in a high electric field by the tunneling of electrons from the gaseous atoms to a surface.

Field emission, ion, liquid metal–Creation of metal ions by evaporation from a liquid metal wetted point in a high electric field.

Field emitter tip–Sharp point used to generate electrons or metal ions by high electric field effects.

Field evaporation–Vaporization from a sharp tip due to a high electric field.

Film (substrate)–A free-standing flexible structure of limited thickness. Also called a *web*.

Film ions (PVD technology)–Ions of the condensable film material being deposited. Often accelerated to a high kinetic energy in an electric field.

Filtered arc source–An arc vaporization source designed to filter out the macros, generally by deflecting the plasma beam. See *Arc source, Plasma duct.*

Filtration (cleaning)–Removal of a species from a fluid.

Filtration, particle–Removal of particles having a size of one to 100 microns.

Filtration, microfiltration–Removal of particles of 0.1 to 10 microns.

Filtration, ultrafiltration–Removal of particles of 0.001 to 0.1 microns.

Filtration, Reverse Osmosis (RO)–Removal of ionic-sized particles.

Fin (ceramic)–A thin edge formed on a ceramic during the fabrication process. Much the same as a burr except not due to deformation. See *Burr*.

Final rinse (cleaning)–In wet cleaning the surface being cleaned should be kept wet until the final rinse which is the last rinse before drying. This rinse should be done with ultrapure water to a specified resistivity to minimize residues. See *Rinse-to-resistivity*.

Fines–Particles smaller than the average or specified particle size. See *Mesh sizing*.

Finger cots (cleaning)–Coverings, usually of rubber, that only cover the tips of the fingers and can be used instead of gloves when handling material in some cases. Can be used inside cloth gloves.

First surface (optical)–The surface of the optical substrate facing the incident radiation. Example: first surface mirror which is metallized on the "front-side" of the glass. See *Second surface.*

Fisheye (defect)–A flow defect in a flow-coated surface resulting from a particulate or inclusion on the surface.

Fixture (film deposition)–The removable and generally reusable structure that holds the substrates during the deposition process. The fixture is generally moved, often on several axes, by tooling during the deposition process. In some cases the same fixture is used to hold the substrates during the cleaning process. See *Rack, Tooling.*

Fixture, cage (film deposition, electroplating)–A container with wire mesh sides that contains loose parts and is rotated during the deposition process to allow complete coverage of the parts. Also called a *barrel fixture*.

Fixture, callote–A hemispherical cap-shaped fixture on which the substrates are mounted. Often used in thermal evaporation to keep the substrate surfaces an equal distance from the point-evaporation source and keep the angle-of-incidence of the deposition normal to the substrate surfaces.

Fixture, cassette (semiconductor processing)–A storage fixture that hold wafers so that the paddle can perform a pick-n-place motion. See *Paddle*.

Fixture, christmas tree–A fixture that has a number of branches on which parts are hung. Also called a *tree fixture*.

Fixture, carousel–A fixture on which parts are mounted and then moved in a circular motion (like a merry-go-round). Example: in front of a sputtering target or between two sputtering targets.

Fixture, drum–A cylindrical fixture where the substrates are mounted on the walls of a cylinder or mounted on structural members (like a rotisserie) positioned in a cylindrical arrangement.

Fixture, ladder (thermal evaporation)–A fixture for holding a number of evaporator filaments in a vertical array so as to approximate a line source.

Fixture, pallet–A planar surface on which the substrates lie, and which passes under or above the vaporization source. Often the initial angle-of incidence of the depositing material is high which can lead to film-density problems.

Fixture, planetary–A fixture that has a motion around one fixed axis and several moving axes in a plane.

Fixture, vibratory pan–A fixture for coating small parts by placing them in a pan that is vibrated causing the parts to move about and allowing 100% coverage of the part.

Flakes (contamination control)–Particles of film material that become dislodged in the vacuum system and generate particulate contamination in the system.

Flame spray (thermal spray)–Melting small particles in a flame, such as an oxygen-acetylene torch, accelerating the molten particles in a high velocity gas stream (1200 ft/sec) and "splat cooling" them onto a surface.

Flame treatment (polymer)–A method of oxidizing the surface of a polymer web to increase its surface energy by subjecting it to a flame in air. See *Corona treatment, Plasma treatment*.

Flammable gas–A gas which is flammable in a mixture of 13% or less (by volume) with air. See *Flash point*.

Flange (vacuum technology)–A mechanical structure designed to allow sealing of one structure to another, usually to isolate vacuum from the ambient pressure. The flange may provide sealing by use of an elastomer seal, a deformation seal or a shear seal. Often feedthroughs are mounted on the flange. See *Feedthrough*.

Flange, blank-off (vacuum technology)–A flange that does not contain a feedthrough or other component that is used to seal a port.

Flange, sexless (vacuum technology)–A flange whose mate has an identical sealing structure.

Flash (electroplating)–A very thin coating (2.5 microns or 0.1 mils) or less. Often used to prevent corrosion of a surface. Example: flash of gold. See *Strike*.

Flash deburring–The burning-off of a burr in a flame front produced by an explosion.

Flash evaporation (film deposition)–The deposition of a material by rapid heating so that there is no time for diffusion or selective evaporation. Flash evaporation is used to deposit alloy materials where widely different vapor pressures prevent uniform vaporization of the elemental components of the alloy.

Flash evaporation, exploding wire–The heating and vaporization of a wire by the sudden discharge of an electrical current through the wire.

Flash evaporation, laser ablation–Vaporization of a surface by the adsorption of energy from a laser pulse.

Flash evaporation, pellet feed–Where individual pellets are fed onto a hot surface where they are completely vaporized before the next pellet is dropped.

Flash evaporation, wire tapping–Where the tip of a wire is periodically tapped against a hot surface so the tip of the wire is periodically vaporized.

Flash point (safety)–The lowest temperature at which vapors will ignite and burn when exposed to an ignition source. Important consideration when using flammable materials.

Flash rust (cleaning)–The oxide (rust) layer that rapidly forms on the dry, oxide-free surface of steel.

Flaws, interfacial (adhesion)–Flaws in the interfacial material, such as cracks and voids that concentrate stress and provide initiation points for fracture. Their presence lowers the fracture toughness of the interfacial material. See *Flaws, surface*.

Flaws, surface (substrate, adhesion)–Flaws in the substrate surface such as cracks or voids that become incorporated into the interfacial region. Their presence lowers the fracture toughness of the interfacial material.

Flip-chip bonding (semiconductor processing)–When the circuit die is connected directly to the printed circuit board or chip carrier by means of solder bumps. See *Die*.

Float glass (substrate)–Glass sheet formed by continuously pouring molten glass onto a bed of molten tin. Most window glass is made by this technique which leaves a layer of tin oxide on one surface.

Floating potential–The electrical potential assumed by a material that is electrically isolated from ground.

Flocculate (cleaning)–To cause to come together into a mass. Flocculation is performed on turbid water before the purification operation. See *Flocculating agent*.

Flocculating agent (cleaning)–Agent used to cause small particles to coalesce into a large mass. Also called a *flocculant*. Example: used in water treatment prior to filtration.

Flood panel (vacuum technology)–A water-cooled double-walled panel, such as the wall of a vacuum chamber, that is used to remove process heat from the surface.

Flow, laminar (cleaning)–A streamline gas or fluid flow without turbulence.

Flow, mass (vacuum technology)–Particles per second passing by a position. Also called *mass throughput*.

Flow, molecular (vacuum technology)–Gas flow conditions where there are few collisions between molecules because of the long mean free path for collision (low pressure).

Flow, transition (vacuum technology)–Gas flow conditions intermediate between viscous flow and molecular flow where the flow characteristics are determined by molecular collisions and collisions with the walls of the duct.

Flow, turbulent–A gas or fluid flow where local velocities fluctuate in an irregular and random manner. See *Velocity*.

Flow, viscous (vacuum technology)–Gas flow conditions where the mean free path for collision is very small compared to the dimensions of the system.

Flow chart, process (manufacturing)–A schematic diagram of the processing, including inspection, characterization, handling and storage, that a substrate encounters in going from the as-received material to the final product. The flow chart is useful in determining that complete documetaion has been developed for all phases of the processing.

Flow coating (PVD technology)–Coating by flowing a fluid over a surface. Used to apply basecoat material, particularly for producing a smooth surface. Also used to apply liquid topcoat. See *Dip coating.*

Fluid application (cleaning)–The various means of applying a cleaning or rinsing solution to a surface in order to clean or rinse it.

Fluid application, immersion–To leaving in a cleaning solution for a long period of time often with mechanical movement of the part and agitation of the solution. Also called *soaking*.

Fluid application, spray–Spraying with a cleaning or rinsing agent with a Low pressure spray (<100 psi) or a high pressure spray (>1000 psi).

Fluid application, ultrasonic–Cleaning or rinsing using the jetting action of the collapse of cavitation bubbles in contact with a surface to provide agitation. Frequencies in the range of 20 kHz to 100 kHz.

Fluorophores–Fluorescent materials.

Flux (particle bombardment)–The number of particles per unit area per unit time. Example: ions per cm^2 per second. Also called the *dose rate.*

Flux distribution (film deposition)–The angular distribution of the particles incident on the substrate surface.

Flux distribution (vaporization)–The angular distribution of the particles leaving a vaporization source. See *Cosine distribution*.

Flux ratio (ion plating)–The ratio of the number of energetic bombarding particles to the deposition rate of the depositing condensable film atoms.

Fluxing (cleaning)–A metal cleaning technique that operates by dissolving or floating-off the oxides on a surface using a hot molten fluid solvent which is often a borate.

Fogger (cleaning)–Machine for generating fine particles for checking mechanical filters in an air circulation system. See *Dioctyl phthalate (DOP)*.

Footprint (equipment)–The amount of floor space that a piece of equipment occupies.

Forcefill (metallization) (semiconductor processing)–The use of a high isostatic pressure (~60 Mpa) and temperature (~400°C) to close voids in thin film aluminum metallization.

Foreline (vacuum technology)–The plumbing between a high vacuum pump and its backing pump.

Foreline pressure (vacuum technology)–The pressure in the foreline at the outlet of the high vacuum pump.

Forepump (vacuum technology)–A vacuum pump used to keep the discharge pressure of a high vacuum pump below some critical value. The forepump may be also used as a roughing pump by proper valve sequencing. Also called a *backing pump*. See *Roughing pump*.

Forming gas–A gas mixture of nitrogen and hydrogen (usually 90:10) which has a low flammability.

Fourier Transform Infrared (FT-IR) analysis (characterization)–Infrared spectroscopy using the adsorption of infrared radiation by the molecular bonds to identify the bond types which can absorb energy by vibrating and rotating. In Fourier Transform Infrared spectrometry (FT-IR) the need for a mechanical slit is eliminated by frequency modulating one beam and using interferometry to choose the infrared band.

Fractional distillation–A means of purifying a material by selective vaporization of the more volatile material(s). Purification may be of the material remaining or of the material volatilized. Used to purify evaporant materials (vacuum evaporation), solvent cleaners and pump oils.

Fractionation, by evaporation (PVD Technology)–When preferential vaporization of one constituent of a vaporizing melt occurs due to its higher vapor pressure leaving the melt with an increasingly higher proportion of the less-volatile material. See *Fractional distillation, Raoult's Law*.

Fractionation, gas, by pumping (vacuum technology)–Changes in the composition of gas in a vacuum chamber due to preferential pumping of one gas species over another. Example: cryopumping increases the relative helium content in the chamber since it pumps helium poorly.

Fractoemission (adhesion)–The emission of electrons during the fracture of a dielectric, brittle solid due to charge separation and arcing. Also called *exoemission*.

Fractograph–The picture of a fractured surface.

Fracture (adhesion)–The generation of two free surfaces through the bulk of a material or at an interface between materials.

Fracture initiation (adhesion)–The starting point of a fracture. Often fracture, particularly in a brittle material, starts at a flaw or point of stress concentration. The amount of stress that must be imposed to initiate a fracture when there is no flaw present. The stress needed to initiate a fracture is usually much higher than that needed to propagate the fracture.

Fracture propagation (adhesion)–The extension of a fracture through the material.

Fracture toughness (adhesion)–A measure of the amount of energy needed to cause fracture propagation.

Fragment pattern (mass spectrometry)–The portion of the spectra from a mass spectrometer due to the breaking up of complex molecules by electron bombardment. Also called a *cracking pattern*. See *Fragmentation*.

Fragmentation (plasma technology)–Breaking a molecular species up into less complex species.

Frank-van der Merwe growth mode (film formation)–Layer-by-layer growth where there is strong interaction between the depositing atoms and the substrate. Complete coverage of the substrate is attained in a few monolayer film thickness. See *Volmer-Weber (island) growth, Stranski-Krastanov (pseudomorphic) growth*.

Free energy, surface–The energy per unit surface area which results from the asymmetrical bonding of the surface atoms. See *Surface tension*.

Freeboard ratio–The ratio of the height of the freeboard above the vapor level, to the closer horizontal liquid dimension in an old-style vapor degreaser.

Fretting wear (contamination control)–A type of wear where adhesion between two contacting surfaces in relative motion causes the wear.

Friction (vacuum technology)–The resistance of surfaces in contact to move relative to each other. The higher the friction the more likely the galling and generation of particulate contamination. See *Coefficient of friction*.

Frictional drag (vacuum technology)–The deceleration force applied to a moving surface by a gaseous environment in contact with the surface. See *Molecular drag pump*.

Front-end (semiconductor processing)–Equipment and processes that are used to fabricate a wafer. Example: Ion implantation machine, PECVD equipment, Chemical-Mechanical Polishing (CMP) equipment. See *Back-end*.

Frost (vacuum technology)–The solid condensed material that forms on cold surfaces and reduces the thermal conduction from the cold surface to the surface of the frost. The frost is removed by regeneration.

Full flow (leak detection)–When all of the helium passes through the leak detector whose pump has replaced the backing pump of the vacuum system.

Fused salt electrodeposition (electrodeposition)–Electrodeposition using a fused salt, such as a chloride or fluoride, as the electrolyte. See *Metalliding*.

Fused salt metalliding (electrodeposition)–Deposition of a film or coating using fused salt electrodeposition. Often the deposited material reacts extensively with the substrate surface forming an alloy or compound. See *Fused salt electrodeposition, Metalliding*.

Fusion coatings–Coating a surface by fusion of the additive material to the surface. Example: enameling, Thick film metallizing. See *Thick film metallization*.

Galling (contamination control)–Surface damage due to adhesion and fracturing of surfaces in contact. Galling is a source of particulate contamination in vacuum systems containing moving parts.

Galvanize–The process of depositing zinc on a surface usually by hot dipping.

Galvanic corrosion–Electrochemical corrosion due to the voltage generated by dissimilar metals in contact with an electrolyte present. Example: galvanic corrosion between a film matrix and a precipitated phase (Al_2Cu in Al metallization), or chromium carbide in an alloy matrix in stainless steel weldments.

Garnet–A naturally occurring abrasive material which is composed of metal silicates.

Gas–A state of matter in which the molecular constituents move freely and expand to fill the container which holds it. Generally the term includes vapors. See *Vapor*.

Gas, ideal–A gas that is composed of atoms and molecules that physically collide but otherwise do not interact. Low pressure gases are generally treated as Ideal gases.

Gas, non-ideal–A gas that does not obey the ideal gas law because of atomic and molecular interactions other than physical collision. Example: water vapor at room temperature. Also called a *real gas*.

Gas ballasting (vacuum technology)–The introduction of a non-condensing gas into the compression stage of a vacuum pump to dilute the vapors in the pump so that they will not be condensed by compression above their saturation vapor pressures.

Gas blanket–A protective environment formed by an inert gas surrounding the surface.

Gas cabinet (gas distribution)–A storage enclosure designed to provide a controlled local environment to a gas cylinder and to provide safety precautions where needed.

Gas conversion–Forming a hard diffusion layer by heating a surface in contact with a reactive gas which can react with a constituent of the alloy to form a dispersion strengthened layer (case). Example: gas nitridation.

Gas discharge (plasma)–The plasma and associated non-equilibrium regions such as the dark space and wall sheath that are generated by electron-atom collisions, generally due to DC or rf excitation in a vacuum. Also called a *glow discharge* (preferred).

Gas evaporation–Vaporization into a gaseous environment which has a gas density sufficient to allow collisions that lead to gas phase nucleation and the generation of ultrafine particles in the gas. See *Ultrafine particles*.

Gas incorporation (film formation)–Incorporation of soluble or insoluble gases during film growth either by physical trapping or by low-energy implantation by bombarding species. Example: incorporation of helium in gold films. See *Charging, hydrogen*.

Gas scattering–Scattering of a high velocity atom by collision with gas molecules. See *Thermalization, Gas scatter plating*.

Gas scatter plating (film deposition)–Increasing the throwing power of the depositing atoms by scattering the atoms in a gaseous atmosphere. Does not work very well without a plasma due to gas phase nucleation and the deposition of ultrafine particles. When a plasma is present the ultrafine particles become negatively charged and do not deposit on the substrate particularly if the substrate is at a negative potential as in ion plating.

Gas-phase nucleation (particle formation)–The nucleation of atoms in a gaseous environment where multi-body collisions allow the removal of the energy released on condensation. See *Gas evaporation*.

Gaseous arc–An arc formed in a chamber containing enough gaseous species to aid in establishing and maintaining the arc. See *Vacuum arc*.

Gasket (vacuum technology)–The object between sealing flanges that deforms or shears, thus creating the vacuum-tight seal. See *Flange*.

Gate valve (vacuum technology)–A mechanical sealing valve where the motion of the sealing plate is mostly parallel to the plane of the seal. Generally the valve opening is round so that the maximum opening is achieved with the use of the least sealing area. See *Vacuum valves*.

Gauge–A measuring device. Example: vacuum gauge. See *Sensors*.

Gauge–A thickness unit. Example: 18 gauge steel sheet.

Gauge–A diameter unit. Example: 12 gauge electrical wire.

Gauge band (web coating)–A continuous lane of film in the machine direction of the roll that is abnormally thick (hard band) or thin (soft band).

Gauss–Unit of magnetic field intensity equal to one Maxwell/cm^2 or 10^{-4} Weber/m^2. See *Oersted (cgs system), Tesla (SI system)*.

Getter (vacuum technology)–A material that will react with or adsorb reactive gases in the vacuum environment.

Getter (vacuum technology)–To remove gases either by a chemical reaction so as to form non-volatile solid species containing the gas, or by absorption of the gases in the getter material.

Getter pump (vacuum technology)–A vacuum pump that operates by reaction of a surface with the gaseous species to form a non-volatile reaction product or by absorption of the gases into the bulk of a getter material. In reaction-type getter pumps the getter materials are often deposited by evaporation or sublimation. Adsorption-type getter pumps are sometimes called non-evaporative getter pumps. See *Vacuum pump*.

Getter pumping, during deposition (PVD technology)–The gettering action that accompanies the deposition of a reactive film material such as titanium in an oxygen environment.

Gilding–Overlaying a surface with a very thin free-standing film (e.g. gold or silver) which is adhesively bonded to the surface or held to the surface by electrostatic forces.

Glass (substrate)–A non-crystalline material. Generally composed of a mixture of oxides and additives (glass formers) that inhibit crystallization.

Glass, float (substrate)–Glass sheet formed by continuously pouring molten glass on a bed of molten tin. Most window glass is made by this technique which leaves a layer of tin oxide on one surface.

Glass, stressed (substrate)–Glass in which the surface has been put into compressive stress to strengthen the glass by making the generation and propagation of a surface flaw more difficult. The compressive surface region can be generated by thermal quenching or by ion substitution.

Glass bead blasting (cleaning)–Grit blasting using glass beads. See *Shard*.

Glass transition temperature–The temperature above which a brittle glassy material (polymer, oxide glass, etc.) becomes ductile. Also called the *strain point*.

Glaze (coating)–A smooth glassy coating formed by firing a glass frit on a surface.

Glaze (wear)–A smooth surface formed by sliding. See *Burnishing.*

Global Warming Potential (GWP) (cleaning)–A rating for the potential of a vapor to contribute to global warming. See *Ozone Depletion Potential (ODP)*.

Glove box–A controlled-atmosphere box where handling is done with gloves that extend through hermetic seals into the box. Also called *isolators* (England).

Gloves (cleaning)–Hand covering that come into contact with substrates or fixtures and solvents. The gloves should have low-extractables as far as the solvents are concerned. See *Finger cots*.

Glow bar (PVD technology)–A high voltage electrode that allows a glow discharge to be established in a vacuum chamber for cleaning and surface treatment purposes. The glow bar should be as large as possible in order to generate as uniform a plasma as possible throughout the chamber.

Glow discharge (plasma)–The plasma and associated non-equilibrium regions such as the dark space and wall sheath that are generated by electron-atom collisions, generally due to DC or rf excitation in a vacuum.

Glow discharge cleaning–Subjecting a surface to a plasma of an inert or reactive gas to enhance desorption of gases and, in the case of reactive gas plasma, by forming volatile species that leave the surface. Cleaning occurs by the action of ions accelerated across the wall sheath, radiation from the plasma and energy released on the surface by the recombination of ions and electrons. In the cases of reactive gas plasmas, chemical reactions occurs on the surface. See *Ion scrubbing, Reactive plasma cleaning*.

Glow Discharge Mass Spectrometry (GDMS)–An analytical technique where atoms are sputtered from a surface, ionized in the plasma and are then mass analyzed in a mass spectrometer.

Glue-layer (adhesion)–An intermediate layer between the film and the substrate used to increase adhesion. Also called a *Bond coat*. Example: the titanium layer in a titanium-gold metallization on an oxide. The titanium chemically reacts with the oxide and alloys with the gold.

Gold-filled–Gold layer is mechanically bonded (cladded) to the surface by rolling, soldering or drawing. Gold-electroplate or gold-PVD coated items cannot legally be called gold-filled.

Goniometer, contact angle (cleaning, surface treatment)–An instrument for measuring the angle-of-contact of a fluid with a surface using direct observation or projection techniques. See *Contact angle*.

Gowning protocol (contamination control)–The carefully choreographed moves for putting-on (donning) cleanroom clothing (head covering, face covering, bunny suits, booties and gloves) to minimize contamination of the outer surface of the clothing.

Graded interface (film formation)–When the interfacial region between a film and a substrate has composition or properties that vary throughout the thickness. See *Interphase material*.

Grain (gr) (weight)–The smallest unit of weight in the avoirdupois weight system. One grain = 0.0648 grams.

Grain (crystallography)–A volume of material having a specific crystalline composition or a different orientation with respect to its neighboring grains.

Grain boundary–The boundary between two crystalline regions that have different grain orientations.

Gram (g) (weight)–A unit of weight.

Gram equivalent weight–The gram molecular weight divided by the valence of the ion of interest. Example: the gram equivalent weight of carbon in the +4 valence state is 3 grams (i.e., 12 divided by 4). See *Normal solution*.

Gram molecular (or atomic) weight–The weight of a compound (or element) in grams. Example: 12 grams of CO_2. See *Mole, Molar solution.*

Green cleaning (cleaning)–Cleaning using environmentally benign chemicals and processes.

Grit (cleaning)–A particulate material used in abrasive cleaning and surface roughening. Example: steel shot, fractured cast iron shot, silica sand (sandblasting), alumina, magnesium carbonate. See *Grit size.*

Grit blasting (cleaning)–Removal of surface material (gross cleaning) or roughening a surface by entraining grit in a high velocity gas stream directed onto the surface.

Grit size (cleaning)–A measure of the particle size and size distribution used in abrasive cleaning or grit blasting. Example: 120 grit cast iron grit. See *Mesh sizing.*

Gross cleaning (cleaning)–Cleaning by removal of surface material as well as contaminate material. See *Specific cleaning*.

Ground (electrical)–The electrical plane, usually earth, which has a common zero potential and to which most electrical circuits are referenced by being attached (i.e., grounded).

Ground loop (electrical)–The condition by which an electrical circuit is not attached directly to ground but rather goes through another piece of equipment that prevents the elecrical circuit from being referenced to the ground (zero) potential.

Ground shield (plasma technology)–A grounded surface placed at less than a dark-space distance from a DC cathode surface in order to prevent a glow discharge from forming on the surface. See *Paschen curve*.

Gusset (vacuum technology)–A rib used to strengthen a plate to prevent it from bending under pressure.

Gyro radius (plasma)–The radius of the path that an electron takes in a magnetic field. See *Larmour radius*.

Hall Effect–The development of a transverse electric field in a current-carrying conductor placed in a magnetic field. Hall-effect probes are used to measure magnetic field intensities. See *Drift,* **E X B**.

Halogenated solvents (cleaning)–Solvents containing the halogens (Cl, Fl, Br). See *Chlorofluorocarbon*.

Hard coating–A coating that extends the life of a tool that is subject to wear such as a drill bit, extrusion die, injection mold, etc. The mechanism may not be entirely related to hardness of the coating. For example the coating can reduce the friction and thus prolong tool life or it may provide a diffusion barrier that prevents adhesion and galling.

Hard vacuum (vacuum technology)–See *High vacuum*.

Hard water (cleaning)–Water containing dissolved ions (e.g. Ca, Fe, Mn) that can leave a residue if evaporated or if they react with other chemicals such as phosphates to form water-insoluble compounds. See *Soft water, De-ionized water*.

Hardness–The resistance of a surface to deformation. Generally measured by the resistance to indentation.

Haze (cleaning)–Surface morphology that gives diffuse reflection from an otherwise smooth (specular) surface. Example: haze on a glass surface from a residue.

Hearth (e-beam evaporation)–The water-cooled structure that has a depression called a pocket in which the material to be evaporated is contained. See *Pocket, Skull, Liner, Pocket*.

Heat Affected Zone (HAZ)–The region near a weld joint that is affected by heating during the joining process. Example: the HAZ in high carbon stainless steel that has been welded contains precipitated chromium carbide which can cause problems with galvanic corrosion.

Heat exchanger–A high-surface area device to maximize the heat exchange between two physically separate gas or liquid materials.

Heat of condensation–Heat released by the physisorption or chemisorption of species on a surface. See *Heat of vaporization*.

Heat of reaction–Heat taken up (endothermic) or released (exothermic) during a chemical reaction.

Heat of solution (safety)–Heat released or taken-up during solution. Example: add acid slowly to water to prevent local heating and splattering.

Heat of vaporization–Heat taken up during the vaporization of a molecule from a surface and released on condensation. Example: the heat of vaporization of gold from a tungsten surface equals about 3 eV per atom. See *Heat of condensation*.

Heat mirror–A thin film structure that transmits the visible spectrum while reflecting the near-infrared.

Heating mantle (vacuum technology)–A heating device that conforms to the shape of the vacuum chamber (system) and that is used for baking-out the system. See *Bake-out*.

Helicon plasma source (plasma)–A plasma source in which microwave power is used to accelerate electrons in a gas in the presence of a constant magnetic field. See *Plasma source*.

Helium leak detector (vacuum technology)–A mass spectrometer tuned to the helium peak which is attached to a vacuum chamber and monitors any change in helium concentration in the chamber as helium gas is directed toward the exterior of the chamber.

Hermetic seal (vacuum technology)–An air-tight seal.

Heteroepitaxy–Oriented overgrowth on a substrate of a different material or the same material with a different crystalline structure. Example: silicon on sapphire. See *Homoepitaxy*.

Heterogeneous nucleation (film formation)–Nucleation of one material on a different material. Example: silicon on sapphire. See *Homogeneous nucleation*.

Hideouts (cleaning)–Areas on a surface that are difficult to clean such as cavities, pores or surfaces in close contact.

High Efficiency Particle Air (HEPA™) filter (contamination control)–See *Mechanical filter*.

High energy neutrals (sputtering)–High energy neutral species formed by neutralization and reflection of the high energy bombarding ions during sputtering.

High energy neutrals (plasma chemistry)–High energy neutral species formed by charge exchange processes.

High solids content (polymer coating)–Having a low content of volatile components such a volatile organic compounds (VOCs) in the coating material. See *Volatile Organic Compound (VOC)*.

High vacuum (vacuum technology)–A gas pressure where there is molecular flow, a low particle density and a long mean free path for gas phase collisions. Generally taken as a pressure below about 10^{-5} Torr.

High vacuum (PVD technology)–A gas pressure in which there is no significant amount of gaseous contamination that will affect the deposition process or the properties of the deposited film.

High vacuum pump (vacuum technology)–A device for producing a high vacuum, either by capturing and holding the gases or by compressing and expelling the gases. See *Vacuum pump*.

Hillock (metallization)–A raised mound (bump) on a metallization film often formed on ductile metals during electromigration or when there is a high compressive film stress. See *Bleb*.

History, of materials (substrates, cleaning)–The history of a material includes specification of raw materials, fabrication techniques, storage times and environments, etc. In many cases the history of the material to be coated determines what must be done to clean or prepare the surface. In addition, changes in the history from lot-to-lot can be an unacceptable process variable. See *Outgassing, Outdiffusion*.

Holding pump (vacuum technology)–A small-capacity pump used to maintain the foreline pressure of certain types of high vacuum pumps when the use of the main backing pump is not justified. See *Backing pumps*.

Holidays (electroplating)–Voids in the interface between two materials.

Hollow cathode (plasma)–A cathode with a deep cylindrical cavity or tube such that the electrons are trapped in the cavity and are effective in ionizing gases in the cavity. The cathode can be heated to the point that there is thermoelectron emission (hot hollow cathode). The hollow cathode can be used as an electron source.

Hollow Cathode Discharge (HCD) lamp–A light source using a hollow cathode discharge whose emission spectrum is characteristic of the material of which the cathode is comprised.

Homoepitaxy–Oriented overgrowth of a film on a substrate of the same material. Example: silicon on doped silicon. Also called *isoepitaxy*. See *Heteroepitaxy*.

Homogeneous nucleation–Nucleation of atoms on a surface of the same material. Example: silicon-on-silicon. See *Heterogeneous nucleation*.

Hot cathode ionization gauge (vacuum technology)–An ionization vacuum gauge in which the electrons for ionization are obtained from a thermoelectron emitting filament. See *Vacuum gauge*.

Hot dip galvanizing–Coating of a surface by dipping into a molten bath of zinc.

Hot filament CVD (HFCVD)–Chemical vapor deposition where a hot filament is used to decompose the precursor vapor. Used mainly to deposit diamond and diamond-like-carbon.

Hot Isostatic Pressure (HIP) (sintering)–Pressing of an object uniformly from all directions, usually in a hydrostatic media, at a high temperature. Used to form dense structures from powders.

Hot-wall reactor (CVD)–Furnace where the CVD gases and the substrate are heated by conduction and radiation from the containing structure.

Hot water seal (anodization)–The hydration of anodized aluminum to cause the oxide to swell and seal the pores.

Housekeeping (contamination control)–Efforts to minimize contamination in the processing area. Examples include cleaning of surfaces, reducing clutter, storage in closed cabinets, no dust-catching surfaces such as the tops of cabinets, no spaces under cabinets that are hard to clean, etc.

Humidity–The amount of water vapor in the air. See *Dew point*.

Humidity, absolute–The amount of water vapor in the air as measured in grams per cubic centimeter.

Humidity, relative–The ratio of the amount of water vapor in a gas to the amount it would hold at saturation expressed in percent.

Humidity shift (optical)–The change in optical properties of a material as a function of the humidity of the ambient environment.

Hybrid deposition system (PVD technology)–System using two or more deposition techniques in sequence usually in separate chambers. See *Deposition system*.

Hybrid vacuum pump (vacuum technology)–Vacuum pump that combines more than one pumping mechanism. Example: a turbomolecular pump that has a molecular drag stage.

Hydration–Reaction of water such that the water molecules become an integral part of the chemical structure. Example: anhydrous copper sulfate has the chemical formula $CuSO_4$, but the hydrated copper sulfate has the chemical formula $CuSO_4 \cdot 5H_2O$. See *Anhydrous*.

Hydrocarbon–Material composed of hydrogen and carbon bonded with the C=H chemical bond.

Hydrochlorofluorocarbon (HCFC) solvents (cleaning)–Solvent containing hydrogen as well as chlorine and fluorine. Examples: HCFC-22 ($CHClF_2$), HCFC-124 ($CHClFCF_3$). See *Chlorinated solvents*, *Chlorofluorocarbon (CFC) solvents*.

Hydrogen plasma cleaning (cleaning)–Using a hydrogen plasma to promote reduction reactions or to hydrogenate hydrocarbons thus making them more volatile.

Hydrogen reduction (cleaning)–The reaction of hydrogen with a material so as to give up an electron often resulting in the decomposition of a molecule. Example: hydrogen reduction of a metallic oxide to the metal, releasing water.

Hydrogenate–Add hydrogen to a molecule.

Hydrophilic surface (cleaning)–Water-loving surface. Water will wet the surface.

Hydrophobic surface (cleaning)–Water-hating surface. Water will ball-up and not wet the surface.

Hydrosonic cleaning (cleaning)–Hydrosonic cleaning utilizes hydrodynamically generated pressure waves to create agitation in the fluid-solid interface.

Hydrostatic weighing–Weighing in and out of a fluid of known density. This weight along with the measured volume allows determination of the density of the material.

Hydroxyl (radical)–The OH^- radical.

Hysteresis–The lagging of an effect behind its cause.

Ideal gas–A gas that is composed of atoms or molecules that physically collide but otherwise do not interact. Low pressure gases are generally treated as ideal gases. Also called a *perfect gas*. See *Non-ideal gas*.

Ideal Gas Law (vacuum technology)–An equation in gas kinetics that relates the volume (V), pressure (P) and absolute temperature (T) of an ideal gas ($PV = constant \times T$).

Imine–Class of compounds which have the NH radical (Imine group) attached to a carbon atom with a double bond.

Immersion cleaning–To leave the part in a cleaning solution for a long period of time often with mechanical movement of the part and agitation of the solution. Also called *soak cleaning*.

Immersion plating–When an ion in solution that has a less negative potential than the atom of a solid in the solution spontaneously displaces the atom of the solid and deposits on the solid. Example: Gold (+1.50 volts) plating onto copper (+0.52 volts) ; lead (-0.126 volts) or tin (-0.136 volts) (from solder) plating on aluminum (-1.67 volts). Also called *displacement plating*. See *Electrochemical series*.

Immiscible fluids–Non-soluble fluids.

Impact plating–Coating a surface by transfer of material from impacting particles on the surface. The particles may be at a high velocity or be pounded on the surface by a tumbling action. Also called *mechanical plating*.

Impedence (electrical)–The resistance to flow of a current due to the ohmic resistance and the effects of inductance in the circuit.

Impedance matching, rf (plasma)–Matching the impedance of the load (plasma and electrode) to the impedance of the power supply in order to increase the power dissipated into the gas and minimize the power reflected back into the power supply.

Impregnation, vacuum–The removal of gases from pores in a material under vacuum, followed by coating the material with a fluid and then letting atmospheric pressure force the fluid into the pores.

Impurities (characterization)–Foreign materials that are present in a material. The impurities may or may not be detrimental or useful. See *Dopant*.

Impurities, major–Impurities in the amount of tenths of a percent or more.

Impurities, minor–Impurities in the amount of parts per thousand to parts per tenth.

Impurities, trace–Impurities in the amount of parts per thousand or less, down to parts per billion.

In situ cleaning (PVD technology)–Cleaning in the deposition system. Examples: ion scrubbing, reactive plasma cleaning, sputter cleaning.

In-chamber contamination (cleaning)–Contamination that occurs in the deposition system during pumpdown and vacuum processing. Example: backstreaming of pump oils into the deposition chamber.

Index of refraction–The phase velocity of radiation in a vacuum divided by the phase velocity in a specific medium, usually vacuum. Example: high index of refraction materials include TiO_2 and ZrO_2; low index of refraction materials include air, SiO_2 and MgF_2. Also called *refractive index*. See *Refraction*.

Induction heating–Heating of an electrical conductor by placing it in a rapidly changing electric field so that the electrical currents are induced in the metal producing Joule (I^2R) heating.

Inductively Coupled Plasma (ICP) source (plasma)–A plasma source where the plasma is formed in a region surrounded by an rf coil that couples energy into the electrons in the plasma.

Inert gas–A gas that has filled electron shells and thus is relatively chemically inert (e.g. He, Ne, Ar, Kr, Xe). Also called a *noble gas*.

Infrared (IR) spectrum–Electromagnetic radiation in the wavelength range of 0.78 to 300 microns.

Infrared pyrometry–Determination of the temperature of a surface by measuring the infrared radiation emitted from the surface. Useful in temperature ranges below where optical pyrometry (color temperature) is used. See *Optical pyrometry*.

Infrared window–Material that has a high transparency for infrared radiation over some portion of the infrared spectrum. Example: sodium chloride, silicon, germanium, potassium bromide (KBr), cesium iodide and high-density polyethylene.

Inhibitor–A chemical used to reduce the rate of a chemical or electrochemical reaction. Example: rust inhibitor.

Inlet pressure (vacuum technology)–The pressure at the inlet port of a vacuum pump.

Inspection, final (manufacturing)–The final inspection before the completed device leaves the production area to ensure that it meets specified requirements. Also called an *acceptance inspection*. See *Process flow diagram*.

Inspection, in-coming (manufacturing)–Inspection of the as-received material to insure that it meets specifications before it enters the processing sequence. See *Process flow diagram*.

Inspection, in-process (manufacturing)–Inspections at various stages of production to ensure that an unacceptable product is not being processed. The information can provide feedback into production processing before too much unacceptable material has been processed.

Installed cost (equipment)–Cost to purchase and install the equipment. See *Cost of Ownership*.

Interface (film formation)–The region of contact between two materials. See *Interphase material*.

Interface, abrupt–The interface that is formed between two materials (A and B) when there is no diffusion or chemical compound formation in the interfacial region. The transition of A to B in the length of a lattice parameter (≈3A).

Interface, combination–An interface composed of several types of materials such as an alloy with a second phase dispersed in it.

Interface, compound–When the interfacial material (interphase material) that has been formed during the deposition of A onto B along with subsequent diffusion and reaction, consists of a compound of A and B such as an intermetallic compound.

Interface, diffusion–When the interfacial material (interphase material) that has been formed during the deposition of A onto B along with subsequent diffusion, consists of an alloy of A and B with a gradation in composition. See *Kirkendall porosity, Interphase material*.

Interface, mechanical interlockng–A "tongue-and-groove" interlocking where the materials "key" into each other at the interface and a fracture that follows the interface must take a circuitous route with greatly changing stress tensors as the fracture propagates.

Interface, pseudodiffusion–An interfacial region where the material is graded, similar to the diffusion interface. Produced by mechanical means such as beginning the second deposition before stopping the first deposition, or by implantation of high energy "film ions."

Interfacial flaws (film formation, adhesion)–Flaws, such as microcracks or voids, that reduce the fracture strength of the interphase material.

Interference, constructive–When radiation from two sources interact with each other such that the amplitudes add together to produce an intense signal. Example: the white band in optical interference patterns.

Interference, destructive–When radiation from two sources interact with each other such that the amplitudes subtract to produce a weak signal. Example: the dark band in optical interference patterns.

Interferometer–An instrument that measures interference effects using either monochromatic radiation and/or white (continuum) radiation.

Interlock (vacuum technology)–A device that prevents a component from operating normally if it does or does not get a signal from a sensor indicating that something is not correct. Example: electrical interlock that prevents a high voltage from being applied to a sputtering cathode unless the system is under vacuum as indicated by a pressure sensor.

Intermetallic compound–A chemical compound composed of two metals one of which is an amphoteric material. Example: Al_2Cu where aluminum is the amphoteric material. See *Amphoteric material*.

Interphase material (adhesion, film formation)–The material at the interface that is formed by diffusion or reaction at the interface between the film and the substrate. The properties of this material are an important consideration in adhesion. Also called *interfacial material*.

Interstitial (crystallography)–A position between normal lattice sites. Example: an interstitial atom of carbon dissolved in a metal lattice.

Intertool transport–Movement between one tooling arrangement and another tooling arrangement. Often between chambers separated by an isolation valve. See *Tooling*.

Ion–An atom or molecule that has an excess (negative ion) or deficiency (positive ion) of electrons. An ion can be multiply charged.

Ion Assisted Deposition (IAD) (film deposition)–Concurrent or periodic bombardment with energetic reactive ions during film deposition. See *ion plating*.

Ion Beam Assisted Deposition (IBAD) (film deposition)–A special case of ion plating where the deposition is done in a high vacuum and the concurrent or periodic bombardment is provided by ions accelerated from an ion gun or plasma source. Also called *vacuum-based ion plating* or *Ion Beam Enhanced Deposition*.

Ion Beam Enhanced Deposition (IBED) (film deposition)–A special case of ion plating where the deposition is done in a high vacuum and the concurrent or periodic bombardment is provided by ions accelerated from an ion gun or plasma source. Also called *Ion Beam Assisted Deposition* (IBAD) (preferred).

Ion beam mixing (adhesion)–The mixing across an interface to increase film adhesion by high energy ions that penetrate through the interfacial region. Also called *interfacial stitching*.

Ion beam sputtering–Physical sputtering using an energetic ion beam from an ion gun in a good vacuum.

Ion Cluster Beam (ICB) deposition (PVD technology)–A deposition process in which clusters of atoms (1000s of atoms) are electrically charged and accelerated to the substrate to deposit with greater than thermal energy.

Ion exchange (water purification)–The exchanging of Na^+ or H^+ ions for positive ions and Cl^- or OH^- ions for negative ions in hard water to produce soft (Na^+, Cl^-) or ultrapure *(H^+, OH^-) water*. See *Reverse osmosis*.

Ion implantation–The physical injection of high energy (MeV) ions into the surface region of a material to change the electrical (Doping) or mechanical properties of the near-surface region.

Ion milling–The machining (removal) of material by sputtering.

Ion plating (PVD technology)–There is no universally accepted definition of the term "ion plating." Ion plating can be defined as a film deposition process in which the growing film is subjected to concurrent or periodic high energy ion bombardment in order to modify film growth and the properties of the deposited film. The term does not specify the source of depositing atoms (sputtering, thermal evaporation, arc vaporization, chemical vapor precursors, etc.) nor the source of bombarding species (plasma, ion gun, plasma source, etc.) or whether the bombarding species is reactive, non-reactive or a "film ion." Other definitions restrict the configuration to using an evaporation source or a DC diode plasma. Also called *Ion Assisted Deposition* (IAD) and *Ion Vapor Deposition* (IVD).

Ion plating, arc–Ion plating where the source of vaporized material is from arc vaporization.

Ion plating, chemical–Ion plating where the source of depositing material is from a chemical vapor precursor species such as CH_4.

Ion plating, reactive–Ion plating in a reactive gaseous environment where a film of a compound material is deposited.

Ion plating, sputter (SIP)–Ion plating where the source of vaporized material is from sputtering of a solid surface.

Ion plating, vacuum–See *Ion Beam Assisted Deposition (IBAD)*.

Ion polishing–Polishing a surface by high-angle sputtering of a rotating surface.

Ion pump (vacuum technology)–A high vacuum pump that operates by sputtering a reactive getter material, such as titanium which then reacts with the reactive gases in the system. Inert gases are pumped by being implanted and buried in the depositing material. See *Vacuum pump*.

Ion Scattering Spectrometry (ISS) (characterization)–A surface analytical technique in which the probing species are energetic ion species with a specific energy and the detected species are reflected ions that have lost specific amounts of energy by collision with the surface atoms.

Ion scrubbing (cleaning)–The desorption of adsorbed species from a surface in contact with a plasma under the action of ions accelerated across the plasma sheath.

Ion source (plasma technology)–A device for generating ions. Often an ion beam is formed by extraction of ions, using a grid system, from a plasma source and the ions are accelerated away from the source. See *Plasma source*.

Ion Vapor Deposition (IVD)–Ion plating generally using aluminum as the film material. Terminology used mostly in the aerospace industry. See *Ion plating*.

Ionic bonding–Chemical bonding between electrically charged ions.

Ionitriding (surface modification)–The bombarding of a hot surface with nitrogen ions in order to inject the nitrogen into the surface and enhance diffusion into the surface to form a hard case. See *Gas conversion, Plasma Immersion Ion Implantation (PIII).*

Ionization–The formation of ions, generally by electron-atom/molecule impact. Other processes, such as penning ionization, can also cause ionization.

Ionization deposition rate monitor (PVD technology)–A deposition rate monitor that compares the collected ionization current in a reference ionizing chamber to the collected ion current from an ionizing chamber through which the vapor flux of the film material is passing.

Ionization gauge (vacuum technology)–A vacuum gauge that uses ion current formed by electron-atom collisions as an indicator of the gas pressure (density). The electrons are formed as secondary electrons from ion bombardment or from a hot thermoelectron emitting filament. See *Vacuum gauge*.

Isentropic process–A process without a change in entropy. See *Entropy*.

Island-channel-continuous (film formation)–The development of a continuous film under Volmer-Weber nucleation conditions where isolated nuclei grow in size, contact each other and then fill-in to form a continuous film.

Isobaric process–A process without change in pressure.

Isolation technology (contamination control)–A set of technologies and procedures that isolate a product from ambient contamination during processing and transportation.

Isothermal process–A process without change in temperature.

Isotropic property (characterization)–A property that is equal in all directions. See *Anisotropic property*.

Issue (document)–A dated version of a document such as a specification.

Jet assembly (diffusion pump)–The arrangement of surfaces in a diffusion pump that imparts a preferential direction to the vapors formed by heating the pump fluid. Also called a *nozzle assembly*.

Jet vapor deposition (film deposition)–An atomistic deposition process where evaporated atoms are introduced into a supersonic jet flow of inert carrier gas that transports the atoms to the substrate surface.

Joule (J)–The SI unit of work, energy, heat impulse and momentum.

Joule heating–Resistive heating given by I^2R where I is the electrical current and R is the resistance of the conductor.

Karat–A unit for defining the purity of gold with 24 karat being pure gold.

Kaufman ion source (plasma)–An ion source that uses a grid system to extract ions from a confined plasma established using a thermoelectron-emitting filament in a magnetic field.

Kelrez™ (vacuum technology)–An elastomer that is more chemically stable than Viton™. Used in plasma etching systems.

Kelvin (K) temperature scale–A temperature scale defined as zero degrees Kelvin being the temperature at which there is no molecular motion and the heat content of the material is zero. The Kelvin degree has the same magnitude as the Centigrade degree. The triple point of water is then 273.16 K. Zero degrees K = -273.16°C and -459.67°F.

Keyholing (metallization, semiconductor)–When the opening of a high aspect ratio hole or trench closes during film deposition before the bottom of the hole or trench is filled. See *Mouse hole*.

KF flange (vacuum technology)–An O-ring sealing flange with a specific clamping configuration. See *MF flange.*

Kinetic energy–Energy due to motion. See *Potential energy*.

Kirkendall porosity (film formation, adhesion)–Porosity which develops in the interfacial region between two materials when the first material diffuses faster into the second than the second diffuses into the first thus producing a loss of mass and formation of voids in the interfacial region. Also called *Kirkendall voids*.

Knob-twiddler (manufacturing)–A person who has a propensity for changing things, often in disregard of the Manufacturing Process Instructions (MPIs).

Knock-down filter (vacuum technology)–Surface used to reduce the velocity of high velocity particles in the exhaust side of an etching or CVD system.

Knoop (HK) hardness number–The expression derived from the force used and the projected area of an imprint obtained by an specifically shaped (ASTM E 384) diamond indenter forced into a surface. Abbreviated HK (formally KHN). $HK = 14{,}229\ P/d^2$ where P = grams force and d = length of long diagonal in microns. See *Vickers hardness number*.

Knudsen cell (PVD technology)–A thermal vaporization source which emits vapor through an orifice from a cavity where the vapor pressure is carefully controlled by controlling the temperature. Used in Molecular Beam Epitaxy (MBE) processing. Also called an *effusion cell.*

Knudsen flow (vacuum technology)–The transition gas flow range between viscous flow and molecular flow.

Knurling–Impressing a design into a surface by deformation using a roller with a hardened surface containing a design in relief. The process results in workhardening the surface. See *Coining.*

Kosher electroplating–Electroplating using kosher additives.

Labile structure (crystallography)–A crystallographic structure that is readily changed by heat or some other process. Also called a *metastable structure*.

Lacquer coating (decorative coating)–The topcoat that is used to give abrasion resistance, color and texture to a decorative coating system. The lacquer is typically applied over a reflective aluminum film deposited by vacuum evaporation which may be deposited on a flow-coated basecoat which creates a smooth surface. See *Basecoat, Topcoat.*

Laminar flow (cleaning)–Gaseous flow in the viscous flow range but with no turbulent mixing.

Lamination–The bonding of two or more layers together, usually by heat and pressure or by using an adhesive.

Langmuir probe (plasma)–A small-area nondisrupting probe that is used to measure the electron density and electron temperature in a plasma.

Larmor radius (plasma)–The radius of the path that an electron takes in a magnetic field. Also called the *Gyro-radius*.

Laser–Term used synonymously with the acronym for Light-Amplification by Stimulated Emission of Radiation (LASER).

Laser ablation (vaporization)–Vaporization by the adsorption of energy from a laser pulse. Also called *laser vaporization*.

Laser Ablation Deposition (LAD) (film deposition)–PVD using laser vaporization as the vapor source. Also called *Pulsed Laser Deposition* (PLD).

Laser enhanced CVD–Increasing the reaction rate using a laser to provide thermal energy by the adsorption of radiation by the substrate or by Photodecomposition of the chemical vapor precursor.

Laser cleaning–Removal of contaminates from a surface using a laser to provide thermal energy by photoadsorption to desorb the contaminate or to vaporize some of the surface.

Laser glazing–A method of rapidly melting and cooling a surface or a film on a surface. Used to densify and smooth the surface and to enhance interdiffusion and reaction.

Laser melt-particle injection–Process where the surface is melted with a laser and metal carbide particles are mixed with the molten pool before solidification.

Laser treatment (glazing, annealing, crystal structure modification)–A method of rapidly heating and cooling a surface in order to densify a surface, refine the grain size, crystallize an amorphous material, etc. Example: laser treatment of an amorphous silicon film to convert it into a polysilicon material.

Latex (cleaning)–Often used synonymously with rubber. Example: latex (rubber) gloves.

Lattice, crystal (microstructure, crystallography)–The regular, periodic arrangement of atoms in a crystalline solid. See *Crystal structure*.

Lattice defects (crystallography)–Discontinuities in the lattice structure such as vacancies, interstitial atoms, substitutional atoms and dislocations.

Lattice parameter (crystallography)–The atomic separation in a crystalline solid. See *d-spacing.*

Lattice misfit (film formation)–When the lattice of the substrate does not have the same spacing as the film material being deposited. Small misfits can be accommodated by lattice strain (strained-layer superlattice). Large misfits cause dislocations in the interfacial region which extend through the film.

Leaching–Preferential chemical removal of one constituent to produce surface depletion of that material and surface enrichment by the remaining material. The resulting surface may be porous or, in the case of metals, may be burnished to densify the surface.

Leak, real (vacuum technology)–A conduction path from the external ambient environment into a vacuum system.

Leak, virtual (vacuum technology)–A conduction path from an internal trapped volume to the main volume of a vacuum system (no connection to the outside ambient environment). Example: void below the bolt in a blind, tapped hole.

Leak detection (vacuum technology)–The process of finding a leak in a vacuum system. See *Helium leak detector*.

Leak rate (vacuum technology)–The amount of gas passing through a leak expressed in Torr-liters/sec.

Leak valve (vacuum technology)–A device used to introduce gas into a system in a controlled manner. See *Valve, vacuum.*

Leak-tight system (vacuum technology)–A vacuum system that has a leak rate less than a specified value using a specific leak-detection gas and defined leak detection techniques.

Leak-up rate (vacuum technology)–The time for the pressure in a system to rise a specified amount with no vacuum pumping taking place. Generally the leak-up pressure range is specified, i.e., from 10^{-4} Torr to 10^{-3} Torr. The leak-up rate is an indication of the presence of outgassing, desorption, virtual leaks and real leaks.

Legs (cleaning)–The flow of a fluid as it avoids contaminated areas on a surface to give thick, often narrow, flow streams.

Lewis acid–A material that acts as an electron acceptor.

Lewis base–A material that acts as an electron donor.

Life-test (characterization)–Evaluation of a function or property under specific conditions that simulate service conditions, in order to determine how long it will function correctly. See *Shelf life*.

Life-test, accelerated (characterization)–Evaluation of a property or function under conditions that will accelerate failure and allow the determination of the activation energy for failure. By using the arrhenius relationship, the failure time under less severe conditions can be calculated provided the activation energy for failure and failure mode remain constant. See *Arrhenius equation*.

Liquid-like behavior, nuclei (film formation)–The ability of nuclei to move and rotate on a substrate surface.

Liquid jet pump (vacuum technology)–A kinetic vacuum pump where the gases are entrained in a stream of fluid. See *Steam jet pump, Verneuli tube*.

Liquid honing–Producing a polished surface by abrasion using fine abrasive particles entrained in a high velocity liquid stream.

Liquidus range–The temperature range between the melting point and the boiling point of a material.

Liquification by compression (vacuum technology)–When compression results in the partial pressure of a vapor exceeding the saturation vapor pressure producing condensation of the excess vapor into a liquid. Example: water vapor compressed to a pressure above 20 Torr at room temperature will liquify the excess vapor.

Limiting foreline pressure (vacuum technology)–The outlet pressure of a pump above which the pumping efficiency of the pump rapidly deteriorates. See *Crossover pressure*.

Liner, chamber (PVD technology)–A removable surface in a chamber used to collect vaporized material and prevent it from depositing on non-removable surfaces.

Liner, pocket (e-beam evaporation)–A crucible-like container that is sometimes used in the pocket of the e-beam evaporation hearth to lower the conductive heat-loss from the melt and to allow easy removal of the charge from the hearth.

Lint (cleaning)–Small particles of organic material usually formed by breaking-off the ends of fibers.

Load, pumping (vacuum technology)–The amount of gas (mass flow) passing through the vacuum pump.

Loading factor (PVD processing)–A processing variable which is the dependence of the processing parameters on the number of substrates, or the total surface area of the substrates being processed.

Log, calibration (manufacturing)–A dated record of who, when and how calibration was performed on a piece of equipment.

Log, maintenance (manufacturing)–A dated record of when and what maintenance was performed on a piece of equipment and who did it.

Log, operation (manufacturing)–A dated record of when a system was used. This together with the maintenance log allows establishing the time between routine cleaning and maintenance operations. Also called a *run log*.

Long-focus electron beam (evaporation)–A high power electron gun that allows heating and evaporation by focusing an electron beam on the surface from a source that is a long distance away and without bending the electron beam. Example: Pierce gun. See *Deflected electron beam*.

Lot (PVD technology)–All of the materials (substrates, source material, etc.) of identical purity, structure, composition, etc., obtained in a single shipment and traceable to a specific manufacturer.

Low carbon steel (vacuum technology)–A low-cost, ductile, non-hardenable iron alloy that contains a low concentration of carbon. Often used for large vacuum chambers. Care must be taken to avoid corrosion (rust) with use.

Low Pressure CVD (LPCVD)–Chemical vapor deposition that is performed in a vacuum.

Low Pressure Plasma Spraying (LPPS)–Plasma spraying that is performed in a vacuum.

Low-e film–A low-emissivity film that is used to reflect infrared energy. Used for energy management in windows either to keep heat out in a hot climate or keep heat in a cold climate.

Low-k film (semiconductor processing)–A low dielectric-loss film.

Lubricant (vacuum technology)–A lubricating liquid or solid material that is vacuum compatible. Example: MoS_2 dry lubricant, silicone greases. Example: graphite is not vacuum compatible as a lubricant.

M classification (contamination control)–Classification of a cleanroom as to the number of particles per cubic meter that have a size greater than 0.5 microns. Expressed as the logarithm of the number to the base 10. See *Class*.

Machine direction (web coating)–Direction that the web is moving. See *Transverse direction*.

Macrocolumnar morphology (film formation)–The large-sized columnar morphology that develops due to the initial surface roughness of the substrate. See *Columnar morphology*.

Macros (arc vaporization)–Molten globules of electrode material ejected under arcing conditions from a solid cathode and deposited onto the substrate giving nodules in the film. See *Filtered arc source, Plasma duct.*

Magnetron–A crossed-field electromagnetic system where the path of electrons accelerated in an electric field is controlled by a magnetic field at an angle to the electric field. In a magnetron tube the electron motion is used to generate microwave radiation (klystron tube). See *Magnetron*.

Magnetron (sputtering)–Sputtering using a crossed-field electromagnetic configuration to keep the ejected secondary electrons near the cathode (target) surface and in a closed path on the surface. This allows a dense plasma to be established near the surface so that the ions that are accelerated from the plasma do not sustain energy loss by collision before they bombard the sputtering target. The closed path can be easily generated on a planar surface or on any surface of revolution. Also called a *surface magnetron*.

Magnetrons, dual unbalanced–Two unbalanced planar magnetrons positioned such that they face each other with the surface to be coated positioned between the two magnetrons. Generally the north escaping field of one magnetron faces the south escaping field of the other magnetron.

Magnetrons, dual AC–Two planar magnetrons that are side-by-side and are alternately the cathode and anode of an AC (< 50kHz) voltage. This arrangement eliminates the disappearing anode effect in reactive sputter deposition.

Magnetron, conical–A magnetron configuration where the target surface is the interior surface of a truncated conical section. The anode is often positioned in the region of the small diameter portion of a doubly truncated cone. Also called an *s-gun*.

Magnetron, hemispherical–A magnetron configuration where the target surface is the interior surface of a hemispherical section. The anode is often positioned around the lip of the hemisphere.

Magnetron, hollow cylinder–A magnetron configuration where the target surface is the interior surface of a hollow cylinder. The cylinder often has a flange at each end to prevent loss of electrons.

Magnetron, planar–A magnetron configuration where the target surface is a planar surface and the magnetic field is in a configuration such that it is round or oval, The sputter-erosion track resembles a "racetrack."

Magnetron, post–A magnetron configuration which is a post, perhaps with flares on the ends (spool), with a magnetic field either axial to the post or in a series of looped magnetic fields around the post. The electrons are confined along the surface of the post and between the flared ends. Also called a *spool magnetron*.

Magnetron, rotatable cylinder–A planar-like magnetron configuration where the target surface is the exterior surface of a hollow water-cooled tube which is rotated through the magnetic field.

Magnetron, unbalanced (sputtering)–A magnetron configuration in which the magnetic fields are arranged so as to allow some of the secondary electrons to escape from the vicinity of the cathode in order to establish a plasma between the target and the substrate.

Mandrel (electroplating, CVD, PVD technology)–A form (substrate) on which a coating is deposited that is subsequently removed, leaving a free-standing structure. See *Vapor forming*.

Manometer, liquid (vacuum technology)–A pressure measuring device that uses a liquid column to measure the pressure difference in two volumes of gas. Often "U" shaped (two legged) with a good vacuum above one of the legs and the gas being measured above the other leg.

Manufacturability–The issues involved in commercially producing an item including patent position, availability of raw materials, availability of components from outside suppliers, availability of suitable manufacturing space, scale-up, costs, etc. See *Scale-up*.

Manufacturing, early–Manufacturing in the early stages where there are numerous experiments to fine-tune the processing parameters and equipment development to improve product yield and throughput. Many changes to the process documentation.

Manufacturing, mature–Manufacturing after the equipment and processes have been optimized and there are few changes to the documentation.

Manufacturing Process Instruction (MPI)–Detailed instructions for the performance of each operation and the use of specific equipment, based on the specifications, that apply to each stage of the process flow. MPIs are developed based on the specifications. See *Process flow diagram, Specifications.*

Manufacturing Safety Data Sheet (MSDS) (safety)–A data sheet available for all chemicals describing the potential safety and health concerns associated with the chemical.

Marangoni principle—The Marangoni Principle states that a flow will be induced in a liquid body where there are different surface tensions. For example, if a surface is wetted by water and is slowly withdrawn from the water, a meniscus will form. If alcohol is present in the atmosphere above the water, the concentration of the alcohol will be greater in the meniscus than in the bulk of the water. This will create a difference in the surface tension of the water, and the water/alcohol mixture will be pulled from the surface into the bulk of the water.

Mask (PVD technology)–A physical cover that prevents film deposition on an area of the substrate surface. The mask may be in contact with the surface or in the line-of-sight from the source to the substrate. See *Moving masks.*

Mask, moving (film formation)–A method of forming a film structure having a specific thickness distribution by using a moving mask to determine the area and time on which the film material is being deposited on specific areas of the substrate.

Mass Flow Controller (MFC) (vacuum technology)–A component that uses the output of a mass flow meter to control the conductance of a valve and thus control the gas flow through the gas manifold. The component is usually located upstream from the deposition chamber but can be located downstream from the chamber.

Mass–A measure of the resistance of a body to being accelerated. Term is often used synonymously with weight but that is not rigorously correct. See *Weight.*

Mass flow meter (MFM) (vacuum technology)–A component that measures the mass flow of a gas through a manifold system, usually by measuring the heat transfer. See *Mass flow controller.*

Mass spectrometer–A device that determines the charge-to-mass (e/m) ratio of ionized species by deflecting them in an electric or magnetic field or by determining the "time-of-flight" between points in an accelerating electric field. See *Partial pressure analyzer, Residual gas analyzer, Quadrapole mass spectrometer.*

Mass spectrum–The output of the mass spectrometer showing the position and height of the ion current resulting from the collected masses with a specific charge-to-mass (e/m) ratio.

Mass throughput (vacuum technology)–The mass (grams per second) or number density (atoms or molecules per second) of gas that passes through a system or component. Also called *mass flow rate.*

Material Safety Data Sheet (MSDS) (safety)–A sheet available from the manufacturer for all chemicals used in the workplace that details the chemical composition, hazards and potential hazards associated with using the material. By law the MSDSs must be made available to the workers exposed to the chemicals.

Material Test Report (MTR) (semiconductor processing equipment)–A document that accompanies each lot of stainless steel tubing that provides the chemical composition, mechanical properties, etc., and is used to determine the welding parameters. See *Orbital welder*.

Maxwell velocity distribution–The statistical velocity distribution of gas molecules at a given temperature showing the variation of higher and lower velocity (energy) particles from the average velocity. See *Boltzmann's constant*.

May–Term used in a Specification or MPI that grants permission. Example: the gloves may be reused. See *Should, Shall*.

Mean free path–The average distance that a molecule travels between collisions with other molecules.

Mechanical activation (cleaning)–Mechanical disruption of the surface barrier layers, such as oxides, to expose the underlying material and increase chemical reaction rates with the surface. Example: brushing with a stiff metal wire brush in the deposition system just prior to film deposition.

Mechanical disruption (film growth)–A means of disrupting the columnar growth mode by periodically deforming the surface mechanically, such as by burnishing.

Mechanical filter (contamination control)–A filter that prevents the passage of particles by having very small holes in the filter media. Example: HEPA filter.

Mechanical interlocking-type interface (film growth, adhesion)–A "tongue-and-groove" interlocking where the materials "key" into each other at the interface and a fracture that follows the interface must take a circuitous route with greatly changing stress tensors. See *Interface*.

Mechanical polishing–Abrasive removal of the high points on a surface.

Mechanical pump (vacuum technology)–A compression-type vacuum pump with moving parts. The term is generally applied to pumps used for roughing or backing (e.g., oil-sealed mechanical pump, piston pump, diaphragm pump, etc.) and not high vacuum pumps (e.g., turbomolecular pumps). See *Vacuum pump*.

Mechanical scrubbing (cleaning)–Rubbing a surface with a cloth or sponge, usually wet or under a liquid. The scrubbing action displaces contamination from the surface but care must be taken that the scrubbing action does not result in abrasive transfer. To avoid abrasive transfer the rubbing pressure should be controlled. See *Abrasive transfer*.

Mechanical working (forming)–The shaping of metals by deformation such as rolling, forging or extrusion (this type of processing generally creates a texture to the grain orientation).

Mechanical working (fatigue)–The fatiguing of a metal by periodic mechanical deformation.

Medical air–Pure air with no oils or other contaminants that would affect the lungs of an individual breathing the air. Used when compressed air is desired as the processing gas. Also called *SCUBA* (Self Contained Underwater Breathing Apparatus) air.

Medium vacuum (vacuum technology)–The pressure range between rough vacuum and high vacuum.

Megasonic cleaning (cleaning)–Cleaning by high frequency (>400kHz) pressure waves in a fluid where there is no cavitation. The cleaning action is due to frictional drag of the fluid moving over the surface. Used in cleaning flat surfaces such as wafers in semiconductor processing.

Melt (phase change)–Convert from a solid to a liquid.

Melt (material)–A specific lot of material made by melting. Example: melt # of stainless steel.

Melt smoothing (surface modification)–Smoothing of a surface by melting since the molten surfaces tends to become smooth by surface tension effects.

Mer–The repeating structure unit in a polymer.

Mesh sizing–Obtaining particles with a specific size distribution by passing the particles through a series of screens having a specific number and size of openings per square inch. Particles that pass through one mesh but not the next, have a specific size range.

Metallic bonding–The chemical bonding resulting from metallic ions being immersed in a continuum of electrons. See *Chemical bond.*

Metalliding (electroplating)–Electroplating in a high temperature molten salt bath where the deposited material diffuses into the surface of the part.

Metallization (general)–Application of a metal film to a non-conductive surface.

Metallization (electronics)–Application of an electrically conductive film to a nonconductive surface.

Metallization (decorative)–To apply a metal film, usually aluminum, to a low cost part often a molded plastic or a zinc die cast part. Also called *junk coating*.

Metamerism (optical)–Obtaining the same color from two different spectra.

Metastable state–A state which can easily be changed. Example: metastable excited state, metastable crystallographic structure.

Methane (CH_4)–A gas that is used as a chemical vapor precursor for carbon in reactive deposition processes.

MF flange (vacuum technology)–An o-ring sealing flange that uses a specific clamping configuration.

Mho–A unit of conductance equal to the reciprocal of the resistance in ohms. See *Siemens*.

Micelle (cleaning)–A cluster or aggregate of molecules. Example: surfactant molecules agglomerating into micelles.

Microcolumnar morphology (film formation)–The morphology that develops with thickness due to the development of surface roughness due to preferential film deposition on high points on the surface. The columnar morphology resembles stacked posts and the columns are not single grains. Also called *columnar morphology* (preferred). See *Macrocolumnar morphology*.

Micron (length)–Micrometer or 10^{-6} meter, 10^3 nanometers, 10^4 angstroms.

Micron (pressure)–Pressure unit equal to 10^{-3} Torr.

Microstructure (film)–The crystallography, grain size, phase distribution, lattice defect structure, voids, etc., of a film as determined by using an analytical technique such as Transmission Electron Microscopy (TEM). See *Morphology, film*.

Microwave–There is no sharp distinction between microwave frequency and radio frequency (rf) waves or infrared radiation but typically microwaves are in the 1 to 100 gigahertz (GHz) range with a wave length shorter than about 30 centimeters. A common industrial microwave frequency is 2.45 GHz.

Mil–One thousandth of an inch.

Mill finish (metal)–The finish on a metal as it emerges from the fabrication mill. Example: mill oxide scale.

Mirror–A smooth surface that has spectral reflectivity and no distortion of an image on reflection.

Mirror-grade glass–A glass that is flat enough to give no visual distortion of the reflected image when coated to make a mirror. The glass will also have no defects such as seeds and stones.

Miscible–Soluble.

Modified surface–A surface which has properties different than the bulk and the bulk material is detectable in the modified surface. Surface modification can be done chemically, electrochemically, mechanically, etc. Examples: anodized aluminum, shot-peened surface.

Modulus of elasticity–The ratio of the applied tensile stress to the resulting elastic strain Also called *Young's Modulus*.

Molar solution (cleaning)–A solution that contains one mole (gram-molecular weight) of the solute in one liter of the solvent. See *Chemical solution, strength of.*

Mold release (cleaning)–A coating applied to a mold to minimize adherence between the mold surface and the molded part. The mold release is often a silicone and leaves a contaminant on the surface of the molded part that is very difficult to remove.

Mole (mol) (chemistry)–The amount of a material whose mass in grams is equal to the molecular weight. Also called *gram molecular weight.*

Mole (mol) (chemistry)–The amount of a pure substance that contains 6.023×10^{23} chemical units (atoms or molecules). See *Avagadro's Law*.

Molecular Beam Epitaxy (MBE)–The epitaxial growth of a single-crystal film produced in a very good vacuum using a well controlled beam of atomic or molecular species which is usually obtained by thermal evaporation from an effusion cell. See *Knudsen cell*.

Molecular drag pump (vacuum technology)–A kinetic vacuum pump in which velocity is imparted to the gas molecule by contact with a high velocity surface. See *Vacuum pump*.

Molecular flow (vacuum technology)–Flow condition where there are few collisions between molecules because of the long mean free path for collision (low pressure).

Molecular sieve (vacuum technology)–An adsorbent material characterized by a high surface area formed by having many small pores of a well defined size. See *Zeolites, Activated carbon.*

Molecular trap (vacuum technology)–A trap filled with an sorbant for the vapor to be trapped.

Molecule–A group of atoms held together by chemical bonds and that has defined chemical properties. Often used in a context which includes atoms.

Molten salt electroplating–Electroplating where the electrolyte is formed using molten salts (chlorides, fluorides) as the solvent. See *Metalliding*.

Molten salts (cleaning)–Molten salts (chlorides, fluorides, borides) used for fluxing. See *Fluxing*.

Momentum, particle–A vector quantity equal to the mass (m) times the velocity (v) of the particle.

Monolayer (ML)–A single layer of atoms or molecules on a surface in a close-packed arrangement.

Monomer–A material consisting of simple molecular units (mers) that are capable of combining with other mers to form a polymer in which the monomer is a recognizable unit. See *Polymer, Mer*.

Morphology, bulk (film growth)–The properties of the bulk of the film that can be visualized by fracturing the material and then observing the morphology of the fracture surface.

Morphology, surface (film growth)–The properties of a surface such as roughness, porosity, long and short-range features, etc., that can be seen using an optical microscope or Scanning Electron Microscope (SEM).

Mouse hole (film growth)–Void left at the corner of the bottom of a trench during film deposition due to the top closing before the bottom is filled. Caused by geometrical shadowing. See *Keyholing.*

Movchan Demchishin (MD) diagram (film growth)–Structure zone model of atomistically deposited vacuum condensates. See *Structure Zone Models (SZM)*.

Multi-layer film (PVD technology)–A film structure that contains two or more discrete layers of two or more different materials. Many layers can be formed by alternating deposition between vaporization sources. Examples: An X-ray diffraction grating of W-C-W-C…C-W, and Ti-Pd-Cu-Au metallization.

Multi-stage vacuum pump (vacuum technology)–A vacuum pump with two or more stages in series within a single housing. See *Vacuum pump*.

Mutagenic (chemical)–A chemical that has been shown to cause gene mutation in mice.

NaK (contamination control)–A sodium (20-50%) and potassium alloy that is liquid at room temperature and is used to getter oxygen and moisture in an inert gas dry box.

Nanoindentation (characterization)–Indentation of a surface using a very light load. Used to deternine the hardness of a film.

Nanometer (nm)–A unit of length equal to 10^{-9} meters or 10 Angstroms.

Nanophase material–Dense, ultrafine-grained material, often formed by atomistic vaporization processes, that has a high percentage (up to 50%) of its atoms at grain boundaries. Also called *nanostructured material*. See *Ultrafine particles.*

Near-surface region (ion bombardment)–Region near the surface that is below the penetration region of the ions but which is affected by the bombardment by heating diffusion, etc. See *Altered region.*

Nebulizer–Device for producing a fine spray of liquid droplets. Example: Ultrasonic nebulizer.

Negative glow region (plasma)–The bright region at the edge of the dark space in a DC glow discharge.

Negative ion–A particle that has one or more excess electrons.

Neutralizer filament (ion gun, plasma source)–An electron emitting filament used to inject electrons into the ion beam that has been extracted from an ion gun, in order to eliminate "space charge blowup" of the ion beam. Essentially changes the ion beam into a plasma beam.

Newton (N)–The SI unit of force.

Nichrome™ (material)–Tradename for the alloy 60Ni:24Fe:16Cr:1C. Often used for metallization and for resistively heated wires.

Nitric oxide (NO)–A good source of free oxygen that is easier to decompose than O_2.

Nitriding–Formation of a dispersion-hardened surface region by diffusion of nitrogen into a metal-alloy surface containing a material that will form a metal-nitride dispersed phase.

Noble species–An elemental species that has filled valence electron shells and thus is relatively chemically inert (e.g. He, Ne, Ar, Kr, Xe, Au). See *Inert gas*.

Nodule (film growth)–A visual mass of material that has a different appearance, microstructure and/or morphology than the rest of the film material.

Non-aqueous cleaning–A cleaning procedure that does not need water during any portion of its use. See *Semi-aqueous cleaning, Aqueous cleaning*.

Non-aqueous electrolyte (electroplating)–An electrolyte formed by having a non-aqueous liquid solvent such as a fused salt.

Non-aqueous electroplating–Electrodeposition of reactive materials such as aluminum using a non-aqueous electrolyte.

Non-destructive adhesion test (adhesion)–A test that can be performed to establish the presence of a specified amount of adhesion without destroying the film. Example: tape-test of a mirror surface, pull-to-limit wire-bond test. See *Adhesion test*.

Non-linting material (cleaning)–A material that does not produce lint and is suitable for use in a cleanroom.

Non-permanent joints (vacuum technology)–Vacuum seals made so as to allow easy disassembly. The seal is made using an elastomer, a deformation metal seal, a shear gaskets or some other reusable or disposible material. See *Permanent joints*.

Non-polar molecule–A molecule that does not have any permanent electric dipole. Example: oil.

Non-reactive deposition (film deposition)–Deposition where the material that is deposited is the same as the material that is vaporized. Usually performed in a vacuum or inert gas environment.

Non-removable surfaces (vacuum technology)–The surfaces, such as chamber walls, that are not easily removed and must be cleaned in place. See *Removable surface*.

Normal glow discharge–A DC glow discharge in the pressure range that the current density on the cathode (cathode spot) is constant as the pressure changes. See *Abnormal glow discharge*.

Normal (N) solution (cleaning)–Solution containing one gram equivalent weight of material per liter of solvent. See *Chemical solution, strength of*.

Nozzle assembly (diffusion pump)–The arrangement of surfaces in a diffusion pump that gives the preferential direction to the vapors formed by heating the pump fluid. See *Jet assembly*.

Nucleation (film formation)–The stage of film formation where isolated nuclei are being formed on the substrate surface before the film becomes continuous.

Nucleation, de-wetting growth–When nuclei on a surface grow by adatoms avoiding the surface and the nuclei growing primarily normal to the surface. Example: gold on carbon. See *Wetting growth*.

Nucleation, wetting growth–The lateral growth of nuclei on a surface due to the strong interaction of the adatoms with the surface. See *De-wetting growth*.

Nucleation, homogeneous–Uniform nucleation (nucleation density) over the whole surface.

Nucleation, inhomogeneous–Nucleation density varies from place-to-place on the surface.

Nucleation density (film formation)–The number of nuclei per unit area on the substrate surface.

Nucleation sites, preferential (film formation)–Positions on a surface that have a high chemical reactivity and will react with mobile adatoms more readily than most of the surface. The site may be due to chemistry or morphology. Example: steps in the surface providing a high coordination at the base of the step; inclusion of tin in one surface of float glass.

Nuclei, condensation (film formation)–The grouping of mobile atoms (adatoms) on a surface to form a stable structure. Stable nuclei can range in size from a few atoms (strong chemical bonding between the atom and the surface) to many atoms (weak interaction).

Nude gauge (vacuum technology)–A vacuum gauge that is inserted into the chamber volume and has no envelope or tubulation.

Number density (gas)–The number of gas molecules per unit volume.

Oersted (O_e)–Unit of magnetic field intensity. Earth's magnetic field has a strength of about 0.5 O_e. See *Gauss*.

Off-cut surface (substrate)–See *Vicinal surface*.

Off-plating (electroplating, cleaning)–The removal of material from the anode in an electrolysis cell.

Ohm (characterization)–A unit of electrical resistance. See *Sheet resitivity.*

Ohm-centimeter (Ω-cm)–A unit of bulk electrical resistivity (ρ). Example: The resistance *R*, in ohms, of a wire having a length *L*, a resistivity of ρ and an crossectional area of *A* is given by $R = \rho L/A$.

Ohms-per-square (characterization)–Resistivity unit used for thin film structures. See *Sheet resistivity.*

Ohmic contact (metallization)–A low-resistance, non-rectifying electrical contact between a film and a substrate.

Oil mist accumulators (vacuum technology)–A trap to prevent the loss of oil through the exhaust system. Also called an *exhaust trap* or *demister*.

Oil-free vacuum pump (vacuum technology)–Vacuum that doesn't use oil for sealing or lubrication in a way that might contaminate the processing chamber. Also called a *dry pump*. See *Vacuum pump*.

Oil-sealed vacuum pump (vacuum technology)–A vacuum pump that uses oil to seal the space between moving surfaces.

Oleophilic wick (cleaning)–An oil-loving fabric used to skim oil from surfaces.

Open, electrical (semiconductor technology)–Where a portion of an electrical conductor stripe is missing. Detectable by voltage-contrast techniques in an SEM.

Open porosity (substrate)–Interconnected pores that provide a path from the interior of the material to the surface. See *Closed porosity*.

Operational spares (vacuum technology)–Spare parts to replace parts which, if they fail, will prevent use of the equipment. Example: spare roughing pump, spare o-rings.

Operator (manufacturing)–The person operating the equipment, performing the process or implementing the MPIs. See *On-floor training, Formal training*.

Ophthalmic coatings–Coatings on eyewear such as sunglasses.

Optical adsorption spectroscopy (process control)–Characterization of a gaseous medium by measuring the adsorption of a spectrum of radiation as it passes through the gas or vapor. Characteristic wavelengths are adsorbed by the gas and the amount of adsorption depends on the number density of atoms along the pathlength. Can be used as a vaporization rate monitor.

Optical coating(s) (optics)–Single and multilayer film structures used to obtain desired transmittance and reflectance of radiation from surfaces. The property may be due to the intrinsic property of the material (e.g. an aluminum reflector) or due to interference effects. A multilayer optical coating is also called an *optical stack*.

Optical coating(s) (decorative, security)–Single and multilayer film structures used to obtain desired visual effects such as color, texture, light scattering, etc.

Optical coating(s), active–Film structures that change optical properties under an external stimulus.

Optical Density (OD) (characterization)–The logarithm of the ratio of the percent of visual light transmitted through the substrate without metallization, to the percent of visual light transmitted through the metallized substrate. Example: 1% transmission is an OD = 2.

Optical emission (plasma)–The emission of radiation from a plasma due to de-excitation of excited species.

Optical emission spectroscopy–Technique of measuring the optical emission from a plasma. Used to determine the species and density of particles in a plasma.

Optical pyrometry–Determination of the temperature of a surface by observing its color temperature, usually by comparing its color to the color of a surface at a known temperature. See *Infrared pryometry*.

Optical spectrum–The visible and near-visible wavelengths (light). The extreme limits are taken as 0.1 microns in the ultraviolet and 30 microns in the infrared. See *Visible radiation*.

Optical thickness (optics)–The product of the physical thickness and the index of refraction of the thin film.

Optically Stimulated Electron Emission (OSEE) (cleaning)–Electron emission from a metal surface under ultraviolet light radiation. Changes in OSEE can be used to quantify surface contamination.

Optically Variable Device (OVD)–A device that presents a different picture when viewed from different angles. Often used as a security measure.

Orange peel (surface)–A uniformly rough, pebbly-looking, surface morphology that resembles the surface of an orange. Often seen on smooth polished surfaces or cured polymer surfaces.

Orbital welder (semiconductor equipment)–An automated arc welder that is used to weld the stainless steel tubing in gas distribution systems. See *Material Test Report (MTR)*.

Organic material–Material consisting of mostly hydrogen and carbon.

Orifice, ballast (vacuum technology)–An opening that continuously allows gas from the outside to bleed into the foreline of a pumping system. This prevents suck-back in the case of a power failure. By using dry air into the orifice, moist air is diluted to the point that water vapor is not condensed by compression in the mechanical pump.

Original equipment manufacturer (OEM) (manufacturing)–The outside supplier of processing equipment that conforms to certain specifications. The supplied equipment may be modified to meet special requirements in the manufacturing environment. See *Beta test.*

Outdiffusion (cleaning)–The diffusion of a species from the bulk of a material. Often used to describe mobile materials that do not vaporize when they reach the surface.

Outgassing (cleaning)–The diffusion and volatilization of species from the bulk of a material. See *Desorption.*

Outgassing rate–The amount of gas leaving a surface as measured by Torr-liters/sec-cm^2.

Over-diffusion (adhesion)–When the extent of the interdiffusion of materials causes a weakening of the material in the diffusion zone. Example: weakening by formation of Kirkendall porosity, or by microfracturing due to stresses caused by phase changes in the diffusion zone.

Over-flow rinse tank (cleaning)–Tank containing rinse water that flows off the top to carry away contaminants that float on the surface. This prevents "painting-on" of the contaminants onto the surface as the surface is withdrawn from the tank.

Overlay coatings–Coatings formed by the addition of another material to the substrate surface. The original substrate material is not detectable in the coating. See *Surface modification.*

Oxidation, chemical (cleaning)–Loss of electrons typically by reaction with oxygen, chlorine, fluorine or bromine.

Oxidation cleaning (cleaning)–Removal of contaminant species by oxidation and solution or volatilization.

Oxidizing agent (cleaning)–A material that causes oxidation and is thereby reduced.

Oxygen plasma cleaning (cleaning)–Cleaning in an oxygen plasma where the contaminant is oxidized and vaporized.

Ozone (cleaning)–The molecular form of oxygen, O_3, which is very chemically reactive. Generated in large amounts in a corona or arc discharge at atmospheric pressure. Generated in smaller amounts in short-wavelength ultraviolet radiation and in low-pressure oxygen glow discharges. Used for cleaning.

Ozone cleaner (cleaning)–Gaseous cleaning technique that uses ozone to produce volatile oxidation reaction products such as CO and CO_2 from the oxidation of hydrocarbon contaminants. Also called *UV/O_3 cleaner*.

Ozone Depletion Potential (ODP) (cleaning)–A rating for the potential of a vapor to deplete the atmospheric ozone layer. See *Global Warming Potential (GWP).*

Pack cementation (CVD)–A CVD-type process where the part to be coated is placed in a mixture (Pack) of inert powder and powder of the material to be deposited. The mixture is heated and a reactive gas reacts with the coating powder to form a chemical vapor precursor which decomposes and diffuses into the surface of the part. Used to carburize, aluminize and chromize surfaces.

Paddle (semiconductor processing)–The tooling that slides under and picks up the silicon wafer.

Parameter window (manufacturing)–The limits to a process variable, such as temperature, between which an acceptable product will be produced.

Paramagnetic–A material in which an applied magnetic field will produce magnetization in the same direction (positive magnetic susceptibility) but has no magnetic moment of it's own. Most non-magnetic materials are paramagnetic.

Partial pressure (vacuum technology)–The pressure of a specific gas or vapor in a system. The sum of the partial pressures equals the total pressure. See *Dalton's Law of Partial Pressures.*

Partial pressure analyzer (vacuum technology, reactive deposition)–A device, such as a mass spectrometer or optical emission spectrometer, that is used to determine the partial pressure of each gaseous species in a gas mixture.

Particle, fine (cleaning)–A particle whose diameter is less than 2.5 microns (EPA definition).

Particle, ultrafine (cleaning)–Particle having a diameter less than about 0.5 microns. Generally formed by vapor phase nucleation or the residue from the evaporation of an aerosol. See *Vapor phase nucleation.*

Particulate contamination (cleaning)–Contamination by particulates. A major source of pinholes in thin films either by geometrical shadowing or by holes generated when the particle is dislodged from the surface.

Parting layer–See *Release layer*.

Parylene process–A polymer film deposition process where a monomer is passed through a heated zone where it is polymerized and the resulting polymer (polyparaxylyene) is then condensed onto a surface under very benign conditions.

Pascal (Pa)–A unit of force equal to a Newton per square meter. 6,900 Pa (6.9 kPa) = 1 psi. See *Pressure, units of.*

Paschen Curve–The curve of the breakdown voltage as a function of the product of pressure (p) times the separation (d) (i.e., p x d) for two electrodes (Rojowski-shaped) in a low pressure gas.

Pass box (contamination control)–Two-door container mounted in a wall which allows passing items from one room to another in a controlled manner.

Passivation–Producing a surface layer on a material that decreases its reaction with the ambient. Example: passivating a copper film with a thin layer of gold to allow easy wire bonding; making a thick chromium oxide layer on stainless steel by thermal treatment in very dry air.

Passive film–A film that does not change properties under stimulation. Example: aluminum mirror coating. See *Active film*.

Passive storage (cleaning)–Storage in an environment that has been cleaned in the past but is not actively being cleaned during the storage. See *Active storage*.

Patent, provisional–A temporary patent that establishes a file date for the disclosure. The provisional patent expires at the end of one year at which point a utility patent with disclosures and claims should be filed.

Patent, utility–A document issued by the US Patent and Trademark Office (USPTO) that grants exclusive use of a process, product or composition of material in the United States to the holder of the patent for a period of 20 years after the filing date.

Patina–Term used to describe the weathered look of a metal such as the dark green patina formed on weathered copper. The color of the patina often depends on the composition of the weathering environment.

Penning ionization (plasma)–Ionization of an atom by collision with a metastable atom in an excited state which is of higher energy than the ionization energy of the first atom. Example: ionization of copper (ionization energy = 7.86 eV) by excited argon (metastable excited states of 11.55 and 11.75 eV).

Penning vacuum gauge (vacuum technology)–An ionization vacuum gauge in which the electric and magnetic fields are approximately parallel. Also called the *Phillips ionization gauge*. See *Vacuum gauge*.

Percent solution (solution strength)–The percent, by weight, of a pure chemical in water. Example: A 50% solution of sulfuric acid contains 696.6 grams of H_2SO_4 in one liter of water. See *Chemical solution, strength of*.

Perfect gas–A gas that is composed of atoms or molecules that physically collide but otherwise do not interact. Low pressure gases are generally treated as ideal gases. See *Ideal Gas* (preferred).

Peristaltic pump (CVD)–A liquid pump that operates by creating a wave motion, by constriction and expansion, in a tube carrying the fluid.

Permanent joints (vacuum technlogy)–A vacuum seal that is made so as not be disassembled easily. Examples: weld joint, braze joint. See *Non-permanent joints*.

Permeation–The passage of a gas or vapor through a solid barrier. See *Diffusion*.

Permeation rate–Permeation measured in Torr-liters/sec-cm^2 or grams/sec-cm^2.

Permissible Exposure Limits (PEL) (safety)–Permissible Exposure Limits to hazardous materials (OSHA). See *Time-Weighted-Average (TWA), Short Term Exposure Limits (STEL)*.

Penneyweight–Unit of weight in the Troy Weight System equal to 24 grains or 1.555 grams.

Perchloroethylene (PERC) (cleaning)–The solvent perchloroethylene (CCl_2CCl_2).

pH (Pouvoir hydrogene)–The logarithm of the reciprocal of the H^+ ion concentration of a solution. Very pure water at 22 ^oC has a H^+ ion content of 10^{-7} moles per liter i.e., a pH of 7. A concentration of 0 to 7 is acidic (e.g. a 1 molar HCl solution has a pH of 0; a 0.1 normal H_2SO_4solution has a pH of 1.17) and 7 to 14 is alkaline or basic (e.g. a 1 molar NaOH solution has a pH of 14; a 0.1 normal NH_4OH solution has a pH of 11).

Phase, thermodynamic–The state of matter such as a solid, liquid or gas.

Phase, crystalline (crystallography)–A physically distinct state of matter (solid, liquid, gas, crystalline, amorphous) or portion of matter (grain, crystallite, inclusion, etc.) that can be defined by analytical means (X-ray diffraction, transmission electron microscopy, etc.).

Phase change–The changing from one phase to another due to compositional, temperature or pressure changes.

Phase diagram–A diagram showing the phases of a material or a mixture of materials as a function of temperature and/or pressure and/or composition.

Phosphate conversion (surface modification)–The production of an electrically-conductive metal phosphate on the surface of a metal by wet chemical reaction. Example: use of zinc or manganese acid phosphate treatment of aluminum for corrosion protection. See *Chromate conversion*.

Phosphor–A material that converts an impinging particle radiation, such as electron bombardment, into optical radiation. Example: cathode ray tube (CRT).

Photodesorption–The desorption of species from a surface due to heating by resonant adsorption of the incoming radiation.

Photoelectron emission–Electron emission stimulated by the resonant adsorption of electromagnetic radiation. Example: photoelectric effect.

Photoexcitation–Excitation of an atom or molecule by resonant adsorption of incident radiation.

Photoionization–Ionization of an atom or molecule by resonant adsorption of incident radiation.

Physical sputtering (PVD technology)–Often called just sputtering. The physical ejection (vaporization) of a surface atom by momentum transfer in the near-surface region by means of a collision cascade resulting from bombardment by an energetic atomic-sized particle.

Physical Vapor Deposition (PVD)–The deposition of atoms or molecules that are vaporized from a solid or liquid surface. See *Chemical Vapor Deposition (CVD)*.

Physisorption–The retaining of a species on a surface by the formation of weak chemical bonds (<0.2 eV) between the adsorbate and the adsorbing material. Also called *physical adsorption*. See *Chemisorption.*

Pickling (cleaning)–Removal of large amounts of a surface layer, such as an oxide scale, by chemical means. Example: acid pickling.

Pick-n-place (semiconductor processing)–A robotic motion to take a wafer from one position and place it in another. Example: from cassette-to-cassette.

Pigment–Material added to a paint or ink to produce a color or optical effect. Example: particles derived from an optical interference stack to produce angle-of-incidence color changes in a paint.

Pilot production–Production to evaluate a process flow using full-scale equipment or equipment that can be scaled-up to meet production throughput requirements.

Pinhole (film formation)–A small hole in the film due to incomplete coverage during film growth or from flaking (pinhole flaking). See *Porosity, film*.

Pinhole flaking (contamination control)–Flaking from film built-up on surface aspirates producing particulate contamination in the deposition system.

Pipe diffusion (semiconductor technology)–Rapid diffusion along a dislocation.

Piranha solution (cleaning)–An oxidative cleaning solution based on sulfuric acid and ammonium persulfate. Used to clean silicon wafers.

Pirani gauge (vacuum technology)–A vacuum gauge that uses the resistance of a heated resistor element, which can change due to gas cooling, as an indicator of the gas pressure (density). See *Vacuum gauge*.

Piston pump–A positive displacement vacuum pump that uses the motion of a piston(s) to compress the gas.

Planar magnetron (sputtering)–A magnetron configuration where the target surface is a planar surface and the magnetic field is in a configuration that the oval sputter-erosion track resembles a "racetrack." See *Magnetron*.

Planarization (semiconductor processing)–To smooth a surface, generally by polishing, after filling a via with metallization.

Plasma–A gas that contains an appreciable number of electrons and ions such that it is electrically conductive.

Plasma, augmented–A plasma whose electron density has been increased by the addition of electrons from an external electron source such as a hollow cathode.

Plasma, auxiliary–A plasma separate from the main processing plasma. For example, an auxiliary plasma is needed near the substrate to activate the reactive gas in reactive magnetron sputtering where the main plasma is confined away from the substrate.

Plasma, equilibrium–A plasma that is volumetrically neutral.

Plasma, low-density–A plasma that has a low particle density.

Plasma, strongly ionized–A plasma where most of the gaseous particles are ionized.

Plasma, weakly ionized–A plasma in which only a small percentage (e.g., 0.01%) of the gaseous particles are ionized and the rest of the particles are neutral.

Plasma activation (film formation)–Making gaseous species more chemically reactive in a plasma by excitation, ionization, fragmentation or by the production of new chemical species. See *Reactive deposition*.

Plasma anodization–Oxidation of an anodic surface in contact with a plasma containing oxygen.

Plasma Assisted CVD (PACVD)–See *Plasma Enhanced CVD (PECVD)*.

Plasma cleaning (cleaning)–Cleaning using a plasma environment. The cleaning action can be from desorption (inert gas plasma) or chemical reaction and volatilization (reactive gas plasma).

Plasma compatible materials (plasma technology)–Materials that do not change properties in the presence of a plasma and do not contaminate the plasma. Many organic polymers are not plasma compatible due to their degradation by the UV from the plasma.

Plasma duct (arc vaporization)–A filtered arc source where the plasma is magnetically deflected so that the macros are deposited on the wall of the duct. See *Arc source*.

Plasma Enhanced CVD (PECVD)–Chemical vapor deposition where a plasma is used to assist in the decomposition and reaction of the chemical vapor precursor allowing the deposition to be performed at a significantly lower temperature than when using thermal processes alone. Example: PECVD of phosphosilicate glass (PSG) encapsulating glass at 450°C in semiconductor processing. See *Reinberg reactor*.

Plasma etcher (semiconductor processing)–A vapor etching system that uses a plasma to activate the etchant vapor which then reacts with a surface to form volatile reaction products. Example: BCl_3 plasma etching of aluminum; CF_4 plus O_2 plasma etching of silicon.

Plasma Immersion Ion Implantation (PIII)–A process in which a metallic substrate is immersed in a plasma and pulsed momentarily to a high potential (50-100 kV). Ions are accelerated to the surface from the plasma and before there is an arc-breakdown, the pulse is terminated.

Plasma parameters (plasma technology)–Important plasma parameters are: electron density, ion density, ion charge state distribution, density of neutral species, electron temperature, ion temperature and average particle temperature. Uniformity of the plasma parameters from place-to-place in the plasma can be important in plasma processing.

Plasma polymerization–The conversion of a monomer vapor to a polymeric species in a plasma or on a surface exposed to a plasma. The monomer may or may not be recognizable in the resulting polymer.

Plasma potential–The potential of the plasma with respect to a surface in contact with the plasma which may be grounded, floating or electrically insulating. The plasma potential will always be positive with respect to any large-area surface with which it is in contact.

Plasma source (plasma technology)–A device for generating a plasma. Often a plasma beam is formed using an electron emitting source in a magnetic and electric field. In some cases a plasma beam is formed from an ion beam by adding enough electrons to produce volume neutralization.

Plasma source, capacitively coupled rf plasma–A plasma source where the plasma is formed in a region between two parallel-plate electrodes driven by rf power. See *Reinberg reactor (PECVD)*.

Plasma source, Electron Cyclotron Resonance (ECR)–A plasma source where the microwave energy, which has a resonant frequency of the electron in a magnetic field, is injected into the plasma-generating region through a dielectric window.

Plasma source, gridless end-Hall–A plasma source that uses a thermoelectron emitter and a magnetic field to confine the electrons so as to impinge on gas molecules exiting an orifice.

Plasma source, Helicon–A plasma source in which microwave power is used to accelerate electrons in a gas in the presence of a constant magnetic field.

Plasma source, Inductively Coupled Plasma (ICP)–A plasma source where the plasma is formed in a region surrounded by an rf coil that couples energy into the electrons in the plasma.

Plasma spraying–Melting small particles in a high-enthalpy plasma and a high-velocity gas stream (1200 ft/sec) and "splat cooling" them on a surface. Plasma spraying is a type of thermal spray processing.

Plasma-based ion plating–Ion plating where the substrate is in contact with a plasma. Typically ions are extracted from the plasma to bombard the substrate and growing film. The plasma also activates reactive gases in the plasma during reactive ion plating. See *Ion plating*.

Plasma-deposited films–Films deposited from a plasma using a chemical vapor precursor gas or a monomer as a source of the deposited material. See *Plasma polymerization, Plasma enhanced CVD, Chemical ion plating*.

Plastic deformation–The permanent deformation of a material under a mechanical stress that exceeds its elastic limit.

Plasticizer (contamination)–A low molecular weight, generally organic, material added to polymer resins to make them more fluid and moldable. Plasticizers can be a major source of contamination coming from the bulk of a molded polymer material.

Plug (metallization) (semiconductor processing)–The material filling a hole or via in the structure. Example: CVD tungsten plug.

Plume (laser)–The cloud of vapor that rises from the heated spot during laser vaporization. The cloud adsorbs some of the laser radiation to produce ions and electrons.

Pocket (e-beam evaporation)–The cavity in the water-cooled copper hearth that holds the material to be evaporated in electron beam evaporation. See *Liner*.

Point-of-use (manufacturing)–The point in the processing flow that the material will be used. Example: measuring the electrical conductivity of ultrapure water distributed though a manifold system at the point of use.

Poisoning, target (sputtering)–Reaction of the surface of a sputtering target either with the reactive gas being used for reactive deposition or with a contaminant gas. The reacted layer causes a change in the performance of the sputtering target.

Poisson's ratio–The ratio of the contracting strain in the diameter direction to the elongation strain in the axial direction when a rod is pulled in tension.

Polar molecule (cleaning)–A molecule that has a permanent electric dipole. Example: ionic salts. See *Non-polar molecules*.

Polarization–The process of producing relative displacement between positive and negative charges.

Polarization bonding–Chemical bonding due to polarization of two atoms or molecules. Also called *van der Waals bonding*. See *Chemical bond*.

Polishing, chemical (surface modification)–Increasing the surface smoothness by using a chemical etch that preferentially removes high spots on the surface. Example: polishing aluminum in 10% HCl, polishing stainless steel in a mixture of acids.

Polishing, electropolish (surface modification)–Polishing a surface that is the anode of an electrolysis cell using a suitable electrolyte. Example: electropolishing stainless steel in a phosphoric acid-based electrolyte.

Polishing, mechanical (surface modification)–The use of abrasives of varying sizes to mechanically abrade a surface to increase surface smoothness.

Polishing, of water (cleaning)–Taking ultrapure water that has been used in processing and sending it back through the water purification system by injecting it downstream of the initial stages of purification.

Polishing compound–A material used to smooth a surface or to give the surface a specific texture. Removal of surface material is a secondary consideration. Examples: cerium oxide, chromium oxide, diamond. See *Abrasive compound*.

Polyamide (substrate)–A condensation-type polymer. Polyamides can retain large amounts of water. Example: Nylon™.

Polymer–A material formed of giant molecules formed by the chemical bonding of small chemical units called mers. The bonding may form a linear chain or there may be multiple bonds between monomers to form highly "cross-linked" polymers. See *Copolymer*.

Polyethylene terepthalate (PET) (substrate)–A polymer material used for webs and plastic containers. PET film is a biaxially oriented material that has good transparency, toughness and permeation barrier properties. Example: DuPont Mylar™.

Polyimide (substrate)–A high temperature polymer. Example: Kapton™.

Polypropylene (PP) (substrate)–A polymer material that is used for webs and plastic containers. Less expensive than PET but has less desirable optical properties.

Polysilicates–Three-dimensional polymer of SiO_2 i.e., essentially every silicon atom is bonded to four oxygen atoms.

Polysiloxaines–Three-dimensional polymer of SiO_2 except that 5-10% of the silicon atoms are bonded to one hydrocarbon moiety, usually a methyl or phenyl group.

Polysilsesquioxanes–Three-dimensional polymer with the formula $(RSiO_{1.5})_n$ i.e., every silicon atom is bonded to one hydrocarbon moiety, usually a methyl group or a combination of methyl and phenyl groups.

Porosimetry–Determination of the open pore volume in a material. Example: mercury porosimetry where mercury is hydrostatically forced into the pores and the weight-change measured. Porosimetry can be used in the specification of sputtering targets formed by powder pressing processes.

Porosity, closed–Pore volume that is interconnected and connected to the surface. May or may not affect measured density depending on the measuring technique.

Porosity, film–Open or closed porosity in the deposited film due to the mode of growth, substrate effects, void coalescence or pinhole flaking. See *Columnar morphology, Macrocolumnar morphology.*

Porosity, open (film)–Pores that are not connected to the surface. Affects density measurements.

Porous silicon–A network of nano-sized silicon regions surrounded by void space. Prepared by electrochemical anodization of a silicon surface.

Port, vacuum–An opening through a chamber wall into the vacuum chamber. See *Flange*.

Position equivalency–When all positions on a fixture yield parts that are indistinguishable one-from-another or that lie within an acceptable range of property variation. If position equivalency is not established, the batch can have unacceptable variations in the properties of the coated parts.

Positive column (plasma)–The field-free, luminous region in a DC gas discharge between the negative glow and the anode. The region that allows the use of gas discharges for linear illumination.

Positive displacement vacuum pump–A mechanical vacuum pump that traps a volume of gas, compresses it and displaces it through an exhaust port. See *Vacuum pump*.

Post magnetron (sputtering)–A magnetron configuration which is a post, perhaps with flares on the ends (spool), with a magnetic field either axial to the post or in a series of looped magnetic field around the post. The electrons are confined along the surface of the post and between the flared ends. See *Magnetron*.

Postdeposition treatments (film formation)–Treatments to change the properties of the film after deposition. Example: topcoating, shot peening or burnishing to close porosity.

Postvaporization ionization (PVD technology)–Ionization of the vaporized (sputtered or evaporated) film atoms to form film ions that can be accelerated in an electric field. See *Film ions.*

Potential energy–Energy due to position. See *Kinetic energy*.

Powder coating (substrate)–Coating formed by the deposition of a powder by spraying or electrostatic spraying, generally followed by heating to fuse the particles together and to the surface. The Powder Coating Institute's *Powder Coating Manual* describes the techniques used.

Power, target (sputtering)–The power (watts) or power density (watts/ cm^2) applied to the sputtering target. This process variable, along with gas pressure and gas composition are the parameters most often used to control the sputtering and sputter deposition processes.

Precision–The closeness of agreement between randomly selected individual measurement or test results. See *Repeatability, Accuracy*.

Precision cleaning–Removal of contaminants from a surface to a predetermined level. Also called *critical cleaning*.

Precursor, chemical, liquid (CVD, PVD reactive deposition)–A liquid which acts as the source of the depositing material by containing the elemental constituents of the coating which are released by heating, reduction etc. The liquid is vaporized in a hot chamber and carried into the deposition chamber by a hot carrier gas. Example: $TiCl_4$ whose boiling point (b.p.) is 136.4ºC as a source of titanium.

Precursor, chemical, vapor (CVD, PVD reactive deposition)–A vapor (at room temperature) which acts as the source of the depositing material by containing the elemental constituents of the coating which are released by heating, reduction etc. Example: SiH_4 as a source of silicon, C_2H_2 as a source for carbon.

Preferential evaporation–When one constituent of an alloy vaporizes faster than another because of its higher vapor pressure at a specific temperature.

Preferential nucleation sites (film growth)–Positions on a surface where the mobile adatoms prefer to condense. Example: charge sites, atomic steps, interfaces; and lattice defects such as grain boundaries, substitutional atoms or emerging dislocations.

Preferential sputtering–When one constituent of the surface sputters more rapidly than another leaving a detectable surface enrichment of the low-sputtering-yield material. Note that this layer must be sputtered before the underlying material is exposed so the ratio of the constituents in the vapor is the same as that of the bulk material even though there is surface enrichment.

Preferred orientation (crystallography)–When non-random growth gives the film microstructure a preferred crystal orientation (texture) in some.

Premelting (evaporation)–Melting the evaporant charge while the shutter is closed. This allows degassing of the charge and establishes good thermal contact of the heated surface to the charge material before the shutter is opened and deposition begun.

Presputtering, target (sputtering)–Sputtering a target with a shutter closed or with the substrates out of line-of-sight, to clean the surface of the target. Also called *target conditioning*.

Pressure, gas (vacuum technology)–The force per unit area exerted by gas molecules impinging on a surface. See *Pressure units*.

Pressure, units of (vacuum technology)–The units of force per unit area used to measure gas pressure. It is important in communication to make sure that each individual knows in what pressure units the other person is talking. Example: "We established the plasma at 10^{-3}" (Torr, mbar, Pascals?).

Pressure, units of, bar–One bar of pressure equals 10^5 Pascals. 1 bar = 0.98692 atmospheres = 750.06 Torr. The bar and millibar are pressure units commonly used in Europe. A millibar (mbar) is one thousandth of a bar.

Pressure, units of, Pascals–A unit of pressure equal to a Newton per square meter. 6,900 Pa (6.9 kPA) = 1 psi.

Pressure, units of, pounds-per-square-inch (psi)–A unit of pressure equal to one pound per square inch.

Pressure, units of, Torr (or torr)–A unit of pressure defined as 1/760 of a standard atmosphere. A milliTorr (mTorr) is one thousandth of a Torr.

Preventive Maintenance (PM)–Periodic maintenance performed to reduce unexpected failure of equipment and extend the life of the equipment. This is opposite of "run-to-crash" approach. Example: periodic oil (lubricant or sealant) change.

Primary standard–A unit whose value (e.g. leak rate, resistivity, length, composition) has been established by an accepted authority (e.g., NIST in the USA) against which other units are calibrated. Generally the primary standard must be periodically recalibrated by the authority. See *Secondary standard*.

Printed circuit (PC)–A conductive pattern on an insulating surface which may or may not include active devices such as relays (large) or semiconductor devices (small). If semiconductor devices are applied to the circuit pattern (appliquéd) the circuit is called a hybrid microcircuit.

Process Flow Diagram (PFD)–A diagram showing each successive stage in the processing including storage, handling and inspection. A PFD is useful in determining that there are MPIs that cover all stages of the processing.

Process parameters–The variables associated with the process that must be controlled in order to obtain a reproducible process and product. Example: time, temperature, target power, gas pressure, etc.

Process parameter window–The limits for each process parameter between which a good product is produced. See *Robust process*.

Process review meetings (manufacturing)–Periodic meetings of engineers from the various shifts, managers and persons involved in developing the specifications, to review changes to the specifications and MPIs and to discuss other matters affecting product yield, throughput, quality, etc.

Process sheet–The process sheet which details the process parameters of the deposition run. Also called a *run sheet*. See *Traveler*.

Product throughput–The number of units produced per unit time.

Profilometer, surface–Instruments for measuring the surface morphology and roughness.

Properties, film–Properties of the film that are determined by some specified technique.

Properties, film, functional–Properties that are essential to the desired function of the film such as sheet resistance for conductivity, optical reflectance for mirrors, etc.

Properties, film, stability–Properties that influence long-term performance such as corrosion resistance, residual film stress, etc.

Pseudodiffusion-type interface (film formation)–An interfacial region where the material is graded, similar to the diffusion interface, produced by mechanical means such as beginning the second deposition before stopping the first deposition, or by implantation of high energy "film ions."

Pseudomorphic structure–A crystalline structure that has been altered by stress, solute atoms, etc.

Pull-outs (adhesion)–Regions of the film having poor adhesion and which are pulled out by adhesion tests (tape test, stud-pull test, etc.). Pull-outs leave pinholes.

Pulse plating (electroplating)–The use of a pulsed DC for plating rather than a continuous DC. This allows higher momentary current densities which can affect the coating morphology. In some cases the polarity may be reversed to give off-plating of the part which affects the coating morphology. See *Off-plating*.

Pulsed DC–Long or short duty-cycle DC pulse that have a very rapid rise time of the voltage. The pulses may all be of the same polarity or they may be of alternating polarity.

Pulsed DC, asymmetrical–Pulsed DC with alternating polarity and different amplitudes in the different polarities.

Pulsed Laser Deposition (PLD)–Deposition using laser ablation as the vaporization source. See *Laser vaporization*.

Pump, direct-drive (vacuum technology)–A mechanical pump where the moving parts of the pump are connected to the motor by a rigid shaft (no belt).

Pump capacity (vacuum technology)–The amount of a specific gas that a capture pump, such as a cryopump, can contain and still pump effectively. When this value is exceeded, the pump must be regenerated. See *Regeneration*.

Pump-down time–The time for a vacuum system to reach a specified pressure (base-pressure).

Pumping speed–The volume flow rate through a vacuum pump in liters per second. Also called *pump speed*. See *Mass throughput; Pump throughput*.

Pumping stack (vacuum technology)–The vacuum pumping system consisting of the roughing and high vacuum pumps and associated plumbing.

Pure water (cleaning)–Water formed by reverse osmosis filtration of ions, activated carbon filtering of organics and mechanical filtering of particulates. Often used as a final rinse when ultrapure water is not required. See *Ultrapure water*.

Purge (vacuum technology, semiconductor processing)–To flow a gas (purge gas) through a system to displace and remove gases, vapors and loose particulates that are present.

Pump throughput (vacuum technology)–The mass of gas (or number of molecules of gas) that pass through a pump per unit time (Torr-liters/sec). Also called *mass throughput*.

Purple plague (adhesion)–The color of the fracture surface in an Au-Al interface when the intermetallic Au_2Al is formed.

Pyrolysis–The fragmentation of heavy molecules by heat.

Pyrophoric gas–A gas that will spontaneously ignite if exposed to air at or below 54°C (130°F). See *Flammable gas*.

Quadrapole mass spectrometer–A mass spectrometer that uses a radio frequency electric field between four electrodes to determine which gaseous species with specific charge-to-mass ratio can traverse from the ionizer to the collector. See *Mass spectrum*.

Quality, product (manufacturing)–The ability of a product to meet the customer's expectations based on cost, appearance, performance, lifetime, reliability, etc.

Quality audit (manufacturing)–An internal acessment of all phases of production that lead to a quality product. Includes considerations such as adherence to MPIs, information feedback, operator morale, consideration of suggestions offered by operators, etc.

Quality Control (QC) (manufacturing)–A procedure for monitoring quality and establishing methods for feedback into production.

Quartz–Silicon oxide (SiO_2). Usually meaning the crystalline form of silica. See *Quartz, fused*.

Quartz, fused–The vitreous (glassy) form of quartz.

Quartz Crystal Monitor (QCM) (deposition rate)–Quartz crystal deposition monitors measure the change in resonant frequency as mass (the film) is added to the crystal face.

Quasi-reactive deposition (PVD technology)–Deposition of a compound from a compound source where the loss of the more volatile species is compensated by having a partial pressure of reactive gas in the deposition environment. Example: quasi-reactive sputter deposition of ITO from an ITO sputtering target using a partial pressure of oxygen in the plasma. See *Reactive deposition*.

Racetrack (sputtering)–The pattern that is eroded by sputtering on a planar magnetron sputtering target.

Rack–Structure to hold parts for processing, such as cleaning or electroplating, outside the deposition system. See *Fixture*.

Rack, to–To mount the parts into a rack or fixture (i.e., "to rack them").

Radiant heating (film deposition)–Heating of a surface by radiation from a hot surface. Example: heating of a substrate from a quartz lamp in vacuum.

Radiation-enhanced diffusion–Enhancement of the diffusion rate by radiation damage from heavy-particle irradiation that generates lattice defects in the near-surface region.

Radiation equation–An equation that provides the intensity of radiation from a hot surface. The radiant energy E from a hot surface is given by $E = \delta T^4 A$ where δ is the emittance of the surface, T is the Kelvin temperature and A is the area of emitting surface.

Radiation shield–An optical baffle that is used to contain radiation or prevent radiation from reaching a surface.

Radical–A group of atoms that form an ionic group having one or more charges either positive or negative. Example: the hydroxyl radical OH^-.

Radio frequency (rf)–There is no sharp distinction between radio waves and microwaves but typically rf frequencies start at about 50 kHz and extend to 100 MHz with 13.56 MHz being a common industrial rf frequency. See *Audio frequency, Microwave frequency.*

Radio frequency (rf) sputtering–Physical sputtering, generally of an electrical insulator, where the high negative electrical potential on the surface is achieved by alternately polarizing the surface positively and negatively at a rate greater than about 50kHz. During the positive half-cycle, surface charging is neutralized by electrons from the plasma. During the negative half-cycle, ions are accelerated from the plasma to sputter the surface. See *AC sputtering*.

RF plasma source–A plasma source that uses radio-frequency radiation to excite the plasma. The design may use a coupled plasma such as a parallel plate design or an inductively coupled plasma using a coil design. See *Plasma source*.

Rain (vacuum technology)–Vapor phase condensation of water when a chamber with high humidity air is pumped so fast that the gas temperature is lowered below the dew point.

Random arc (plasma)–Cathodic arc where the arc is allowed to move randomly over the cathode surface. See *Arc source*.

Raoult's Law (evaporation)–Raoult's Law states that constituents of a liquid vaporize at a rate proportional to their vapor pressures.

Rapid Thermal Chemical Vapor Deposition (RTCVD)–Chemical Vapor Deposition using rapid heating and cooling to deposit a coating.

Rapid Thermal Processing (RTP)–Heating process characterized by rapid heating to a high temperature, a short time-at-temperature, then a rapid cool-down. The heating mostly affects the near-surface region. Example: RTP diffusion into a surface.

RCA cleaning process (semiconductor processing)–A cleaning procedure widely used for cleaning silicon wafers. Also called a *modified RCA cleaning process*.

Re-sputtering rate (ion plating)–The rate of sputtering of the depositing film material due to the concurrent energetic particle bombardment of the growing film. Example: about 20 to 40% resputtering is necessary to completely disrupt the columnar morphology of the depositing film material.

Reactant availability (reactive deposition)–The availability and chemical reactivity of the reactive gas over the surface of the film being deposited. Since the surface of the film is continually being buried, reactive gas availability is an important parameter in reactive deposition process.

Reaction probability (reactive deposition)–The probability that a reactive gas species impinging on a surface will react with the surface to form a compound. The probability depends on the reactivity of the species, residence time on the surface, surface coverage, surface mobility, reaction-enhancing processes such as concurrent electron or ion bombardment, etc.

Reactive deposition (film formation)–Film deposition process in which the deposited species reacts with an ambient gas, an adsorbed species or a co-deposited species to form a compound material. See *Quasi-reactive deposition*.

Reactive evaporation (film deposition)–Evaporation in a partial pressure of reactive gas in order to deposit a compound film material. See *Reactive deposition*.

Reactive Ion Etching (RIE) (cleaning)–Chemical etching of a surface under bombardment by low-energy reactive ions that are generally accelerated from a plasma of the reactive gas.

Reactive Ion Beam Etching (RIBE) (cleaning)–Chemical etching of a surface under bombardment by a reactive ion beam from an ion source that is usually collimated and often monoenergetic.

Reactive plasma cleaning (cleaning)–Reaction of contaminants with reactive species to form volatile compounds.

Reactive Plasma Etching (RPE) (cleaning)–Chemical etching of a surface in contact with a plasma of the reactive gas. See *Reactive Ion etching*.

Reactively graded interface (film formation)–A graded interface formed by changing the availability of the reactive gas during the formation of the interfacial region. Example: grading the film composition from titanium to TiN_{1-x} to TiN by changing the availability of the nitrogen during reactive deposition.

Reactor, CVD–The furnace in which the CVD process takes place. See *Reinberg reactor.*

Reactor, cold wall, CVD–Reactor furnace where the CVD gases are heated by the hot substrate and the walls of the containing structure are cold.

Reactor, CVD, fluidized bed–A means of floating, stirring and mixing parts in a heated chamber using a flow of gas containing the chemical vapor precursor. Vibratory action can also be used to aid in moving the parts. Particles can be added to the parts to keep them separated during deposition. See *Pack cementation*.

Reactor, CVD, hot wall–Reactor furnace where the CVD gases and the substrates are heated by conduction and radiation from the containing structure (furnace).

Reactor, CVD, Reinberg–A parallel-plate, rf-driven reactor for plasma enhanced CVD (PECVD).

Real gas–A gas that does not obey the Ideal Gas Law because of molecule-molecule chemical interactions. Example: water vapor at room temperature.

Real surface (substrate)–The substrate surface that must be processed in film deposition. The real surface often has reaction layers, such as oxides, contaminant layers such as adsorbed hydrocarbons and some degree of particulate contamination. Also called *technological surface*.

Recoil implantation (cleaning, film formation)–When a high energy bombarding species imparts enough energy to a surface atom to cause it to be recoil implanted into the lattice as an interstitial atom.

Recombination (plasma chemistry)–The combining of a positive ion with an electron so as to form an uncharged species. This process mostly occurs on surfaces and the process gives up the ionization energy to the surface and the neutral species.

Recommended Practice–A type of specification that has not gone through the rigorous review procedure as that of a Standard. Example: AVS recommended practices for calibrating pump speed. See *Standard.*

Recontamination (cleaning)–The contamination of a cleaned surface. Recontamination depends on the chemical reactivity of the surface, the environment and the exposure time.

Recrystallization–Change of phase or crystal growth orientation in a material due to temperature or stress. Example: devitrification of glass.

Redeposition–When a material that has been vaporized, deposits on the surface from whence it came. Example: backscattering in a gaseous environment.

Reducing agent (cleaning)–A material that adds electrons and elemental species such as hydrogen to a compound, often forming a volatile species. Example: hydrogen reduction of the oxide on a metal surface by dry hydrogen gas to form water and an oxide-free metal surface.

Reduction reaction–A chemical reaction in which a compound gains an electron. Also: the addition of hydrogen or the loss of oxygen.

Reduction reaction (CVD)–Reduction of a chemical vapor precursor to obtain a condensable film material. Example: $TiCl_4 + 2H_2 \rightarrow Ti + 4HCl$.

Reflected high energy neutrals (sputtering)–In the sputtering process, a portion of the high energy bombarding ions becomes neutralized and are reflected from the cathode (target) surface. If the gas pressure is low, these high energy particles are not thermalized and bombard the growing sputter-deposited film and influence film properties such as residual film stress.

Reflected power, rf (plasma technology)–Rf power that returns to the power supply because of poor impedance matching between the load and the power supply. Reflected power should be minimized by proper impedance matching.

Reflow (surface)–Heating a surface to melt and flow the surface.

Refraction–The bending of light as it passes from one media to another because of the change in the velocity of the light in passing from one media to the other.

Refractive index (optics)–The ratio of the velocity of light in vacuum to the velocity of light in a material. Also the sine of the angle-of-incidence of the light beam in vacuum to the sine of the angle-of-refraction of the light as it enters the second media.

Refractory material–A material that has a very high melting point.

Regeneration (vacuum technology)–Warming up a cryosorbing material to cause the adsorbed gases to be volatilized. Regeneration may be to room temperature (activated carbon) or to higher temperatures (Zeolites).

Regeneration cycle time–The time necessary to regenerate the cryosorbing material and to return it to its operating temperature.

Reinberg reactor (PECVD)–A parallel-plate, rf-driven reactor for plasma enhanced CVD (PECVD). See *Reactor, CVD*.

Relative humidity–The ratio of the amount of water vapor in a gas to the amount it could hold at saturation expressed as a percent. See *Humidity*.

Release layer (vacuum technology, PVD technology, electroplating)–A layer (release agent) that ensures poor adhesion between the deposited film and a surface. Used in cleaning excess material from vacuum surfaces and to release a deposit from a mandrel to become a freestanding structure.

Remote region (plasma)–See *Afterglow region*.

Removable surfaces (PVD technology)–Surfaces, such as fixtures, that are routinely removed from the system or surfaces such as liners that can be removed from the system for cleaning. See *Non-removable surfaces*.

Repeatability (manufacturability)–The ability to obtain the same results on a number of trials or measurements. See *Precision*.

Reproducibility–When the process and/or product can be duplicated from run-to-run within specified tolerances.

Residence time (vacuum technology, film formation)–The amount of time that an impinging atom or molecule spends on a surface before it leaves the surface.

Residual film stress (film formation)–The residual compressive or tensile stress in a film that results from the growth process, phase change or differences in the coefficient of thermal expansion of the film and substrate. Not a function of film thickness. Can vary through the thickness of the film and be anisotropic with direction in the film. See *Total film stress*.

Residual gas (vacuum technology)–The gases in the vacuum system at any specific time during pump-down or processing.

Residual Gas Analyzer (RGA)–Device for measuring the species and amount of residual gases in a vacuum system. See *Mass spectrometer, Partial pressure analyzer*.

Residue (cleaning)–Any undesirable material from the chemicals used in processing that remains on a surface after a processing step.

Resistance heating (evaporation)–The Joule or I^2R heating of an electrical current (I) passing through a material having an electrical resistance (R).

Resistivity–See *Sheet resistivity (thin film), Specific resistivity (bulk)*.

Resistivity of water (cleaning)–The electrical conductivity of water as measured between probes spaced one centimeter apart. Example: 18 megohm-cm. One measure of the purity of the water. See *Deionized water, Ultrapure water, Hard water, Soft water*.

Reverse engineering–The process of taking a completed structure and determining the structure, materials and techniques used to build the structure.

Reverse osmosis (water purification)–Using high pressure (600 psi) to force water through a membrane that will not pass ions such as sodium, iron, manganese, calcium, etc.

Rework–To take a part that has been rejected in inspection and repair or redo the reason for the rejection.

Rinse (cleaning)–To remove residual processing chemicals with a material that has no detrimental residue. Example: rinsing with ultrapure water. See *Drag-out.*

Rinse-to-resistivity (cleaning)–Rinsing a surface in pure water until the water retains a specific resistivity such as 10 megohm-centimeters.

Rinsing, cascade (cleaning)–Rinsing using a series of containers (Rinse tanks) having increasingly pure water. Water generally flows over the lip of one container into the next container having a lower purity water. The surface being rinsed goes from the lower purity to the higher purity rinse tank.

Robust process–A process that has wide parameter windows.

Roll coater–See *Web coater*.

Root mean square–The square root of the average value of the squares of the values measured.

Roots blower (vacuum technology)–A compression-type mechanical pump that uses lobe-shaped interlocking rotors to capture and compress the gas. The roots pump uses tight mechanical tolerances for sealing (no oil) and so is sometimes classed as a dry pump. See *Vacuum pump.*

Rotary vane pump–A displacement pump where the compression occurs in a non-symmetric chamber being swept by a rotor having an oil-sealed sliding-vane. See *Vacuum pump*.

Rotatable cylindrical magnetron (sputtering)–A water-cooled tubular sputtering target containing a magnetron magnetic field arrangement such that the wall of the tube is rotated through the magnetic field producing uniform sputter-erosion of the whole surface of the tube. See *Magnetron*.

Rottenstone (abrasive)–A solid block of abrasive that continuously wears during abrasion.

Rough vacuum (vacuum technology)–Pressure from atmospheric to about 50 mTorr.

Rough vacuum (vacuum technology)–Pressure from atmospheric pressure to the crossover pressure. See *Crossover pressure*.

Roughing pump (vacuum technology)–Vacuum pump used to lower the pressure in the system through the rough vacuum range. The roughing pump is often also used as the backing pump for a high vacuum pump. See *Backing pump, Vacuum pump*.

Roughness, surface (R_a)–The arithmetic mean of the departure of the roughness profile from a mean value. The R_a is also called the *Center Line Average* (CLA).

Round-robin (test)–Series of procedures or processes performed by different groups for comparison before the procedure or process is incorporated into a standard. See *Standard*.

Rugate filter (optics)–A film in which the refractive index varies continuously and periodically with the coating thickness.

Run, deposition–Each deposition process including pumpdown-deposition-letup to atmosphere. See *Cycle (process)*.

Rust–Visible corrosion product on ferrous alloys. Usually friable.

Rutherford Backscattering Spectrometry (RBS) (characterization)–A non-destructive technique for depth profiling the chemical composition of a material to a depth of several microns. The probing species is a high energy (MeV) light (He^+) ion and the detected species are energy-analyzed helium atoms that have been scattered from the atoms in the solid.

Sacrificial protection (corrosion)–A form of corrosion protection where one material corrodes in preference to another, thereby protecting it. Example: zinc and cadmium on steel, aluminum on steel.

Sampling method, statistical (manufacturing)–The method used for selecting sample(s) that, when characterized, will be representative of the batch as a whole or for establishing position equivalency on a fixture. Sampling can vary from 100% (such as tape-testing 100% of a mirror surface) to periodic sampling. Sampling is used to characterize the product during the manufacturing process.

Sanitary pipe (vacuum technology)–Elastomer-sealing plastic components used in the food industry which are suitable for use in vacuum technology for some applications such as assembling exhaust manifolds.

Saponification (cleaning)–The conversion of oils into soaps by Alkaline hydrolysis.

Sapphire (substrate)–Single crystal or gem quality aluminum oxide (Al_2O_3). See *Corundum.*

Saturation vapor pressure–The maximum pressure that can be exerted by a vapor in thermodynamic equilibrium with a surface of the material. Example: the saturation vapor pressure of water vapor at room temperature is about 20 Torr. Also called *equilibrium vapor pressure*. See *Supersaturation*.

Scale (cleaning)–A thick layer of oxide that forms on some metals during high-temperature processing. Example: mill-scale on steel directly from the steel mill.

Scale-up (manufacturing)–The ability to increase product throughput to the desired level using proven processes by decreasing the cycle-time, building larger equipment, increasing the operating time, etc. See *Manufacturability.*

Scanning Auger Microscopy (SAM) (characterization)–A scanning surface analytical technique that uses an electron beam as the sampling probe and Auger electrons as the detected species to give the composition of the surface. See *Auger Electron Spectroscopy (AES)*.

Scanning Electron Microscopy (SEM) (characterization)–The SEM uses the secondary electrons from an electron-bombarded surface to form an image of the surface morphology. The magnification can be varied from several hundred diameters to 250,000 diameters with high lateral and vertical resolution.

Scanning Laser Acoustic Microscopy (SLAM) (characterization)–In SLAM a pulsed laser introduces a thermal wave into the material. A discontinuity in the material through which the thermal pulse passes, can give rise to acoustic emission which is then detected.

Scanning Thermal Microscopy (SThM) (characterization)–An AFM which uses a thermocouple junction as the probe tip and which can detect variation in temperature over a surface to a lateral resolution of about 10 nm.

Scanning Transmission Electron Microscopy (STEM) (characterization)–The STEM uses the transmission of electron through a thin film to image the microstructure of the film to a resolution of several Angstroms.

Scanning Tunneling Microscopy (STM) (characterization)–The STM measures the electrons that tunnel between a probe tip and a surface. The system is typically operated in a constant current mode and the movement of the tip is determined to about 0.1 Å.

Scatterometry (characterization)–Scatterometry measures the angle-resolved scattering of a small spot of laser-light incident on a surface. The distribution of the scattered energy is determined by the surface roughness.

Scoring (surface)–The formation of a sever scratch or cut on a film or surface. Often used to provide a source of fracture for breaking brittle materials or pulling a film from the surface.

Screen–A sieve having a screen with a specific opening size to allow classification of particles as to their size. Usually used as a series of screen sizes. See *Mesh sizing.*

Scrubbers (vacuum technology, CVD)–Units placed in the exhaust side of a pumping system to remove particulates and toxic gases. Generally the scrubbers use water to collect particles and chemicals though in some cases the gases are burned to form solids. Example: SiH_4 burned to form SiO_2.

Scum (cleaning)–Layer of contamination that floats on the surface of a liquid. Scum can be removed mechanically (skimming) or by using overflow tanks.

Scum (evaporation)–Material that is on the surface of molten material and that is visually obvious.

Seal, bakeable (vacuum technology)–A seal that can be heated to an elevated temperature, typically 400ºC.

Seal, elastomer (vacuum technology)–A seal using an elastomer to provide the deformation and pressure needed to form a vacuum-tight joint.

Seal, demountable (vacuum technology)–A seal designed to be disassembled and reassembled easily using a gasket. The sealing gasket may be reusable or replaced each time the seal is disassembled. Also called a *non-permanent seal*.

Seal, permanent (vacuum technology)–A seal that is designed so as not to be easily disassembled. Example: A weld or braze joint.

Sealant–Material used to plug a leak.

Sealing surface (vacuum technology)–The smooth surface to which an elastomer gasket deforms and seals.

Second surface coating (decorative coating)–The reflective coating (usually aluminum) that is used underneath the lacquer coating. The lacquer coating (topcoat) is used to give color and texture to the coated part.

Second surface (optical)–The surface of the optical substrate opposite the incoming radiation. Example: Second surface mirror which is metallized on the "backside" of the glass. See *First surface*.

Secondary electron emission–The emission of electrons under electron or ion bombardment.

Secondary Ion Mass Spectrometry (SIMS) (characterization)–A surface analytical technique that uses high energy ions as the probing species and sputtered ions from the surface as the detected species.

Secondary standard–A standard that is commonly used to calibrate components that are in use. The secondary standard is periodically checked against a primary standard at the manufacturing site. See *Primary standard*.

Seed layer (film formation)–A layer, often close to one monolayer thick, that acts as a nucleating layer for subsequent deposition.

Seed (crystal growth)–Single-crystal particle (seed-crystal) that acts to nucleate growth of a single-crystal ingot.

Seed (film formation)–Defect in a deposited film due to particulate contamination of the growing film during deposition.

Seed (glass)–Defect in glass due to a foreign particle.

Seizing (mechanical)–The stopping of moving parts in contact by virtue of galling, deformation, and adhesion.

Selected Area Diffraction (SAD)–Electron diffraction done on selected areas of a film in a Transmission Electron Microscope (TEM) to determine crystal structure.

Selective deposition–Deposition on a local area. May be due to masking, local areas of heating, nucleation sites or local application of electrolyte solutions (brush plating in electroplating).

Self-bias (plasma technology)–An electrical potential on a surface generated by the accumulation of excess electrons (negative self-bias) or positive ions (positive self-bias). See *Sheath potential*.

Self-ion (sputtering, sputter deposition)–An ion of the sputtering target material that can be deposited (also called a *film ion*) or can bombard the sputtering target (self-sputtering).

Self-sputtering–Sputtering by an ion of the target material being sputtered. See *Film ion*.

Semi-aqueous cleaning (cleaning)–Where a non-aqueous material is used for cleaning but water is used in some stage of the cleaning process. Example: a mixture of a terpene with a surfactant for cleaning and water to rinse to remove residue-producing material. See *Aqueous cleaning, Non-aqueous cleaning*.

Semiconductor grade (cleaning)–Materials that meet the purity specifications set by the semiconductor industry.

Semiconductor materials–A material whose electrical conductivity is intermediate between a good conductor and an insulator. The resistivity is generally strongly temperature-dependent and can be varied by doping. See *Dopant.*

Sensitivity (sensor)–The response of a sensor to a small change in the condition being measured. See *Sensor*.

Sensitization (surface)–The production of unsatisfied chemical bonds on a surface which increase the chemical reactivity of the surface. Often sensitization is a temporary condition so the time-to-use must be specified.

Sensor (vacuum technology)–A device that detects a property or condition of a system. The output of a sensor can be used by a microprocessor to control the system. Example: vacuum gauge, temperature gauge, flow meter. See *Feedback*.

Sequestering agents (cleaning)–Materials that react with the metal ions in hard water, keeping them in solution and preventing them from reacting with cleaning agents and forming insoluble precipitates. These materials can present pollution problems if used in large quantities. Example: orthophosphates and orthosilicates.

Serial co-sputtering (PVD technology)–When material from one sputtering target is deposited onto another sputtering target from which it is sputtered to produce a graded or mixed composition.

Set–The permanent or semi-permanent shape that a polymer assumes under a load that relieves the elastic stress in the material. A material, such as Teflon™, that "takes a set" is not a good material for an elastomer seal.

Shall–Term used in a Specification or Manufacturing Process Instruction (MPI) that indicates a mandatory procedure. Example: the gloves shall be discarded after each use. See *May, Should.*

Shaped anodes (electroplating)–Anodes that are shaped (often conformal to the cathodic substrate) to produce a uniform field between the anode and the cathode and to reduce high field regions on the cathode.

Shard (cleaning)–Fragment of a brittle material. Example: glass shards in glass bead blasting.

Shear stress (adhesion)–Stress parallel to an interface. See *Tensile stress, Compressive stress*.

Sheath (plasma)–The region near a surface whose properties are affected by the bias on the surface. Example: wall-sheath, anode-sheath.

Sheath potential (plasma)–The potential across a sheath. Example: the potential across the wall sheath is typically a few eV with the plasma being positive with respect to the wall due to the higher mobility of the electrons as compared to the ions.

Sheet resistivity–The resistance from side-to-side of a square area of any size on a film expressed in ohms-per-square. To obtain the specific resistivity (ohm-cm) of the coating material the film thickness must be known. See *Electrical resistance*.

Sheeting (cleaning)–The uniform flow of a fluid over a surface. If the sheeting is not uniform then contamination is suspected. See *Legs*.

Sheeting agent (cleaning)–A material applied to a surface to cause water to flow (sheet) evenly from the surface. This helps to reduce residues (e.g., water spots) left on the surface. A common sheeting agent is parrafin in a solvent.

Shelf samples–Samples that are placed in a normal environment to age normally and be available for comparison in the future. Also called *archival samples* or *control samples*.

Sherardizing–Coating with zinc by mechanically tumbling a part in hot zinc powder. See *Mechanical plating, Peen plating*.

Short-term Exposure Limits (STEL) (safety)–The short term (15 minutes) exposure limits to hazardous materials as established by OSHA. See *Permissible Exposure Limits (PEL), Time Weighted Average (TWA).*

Shot peening (substrate)–Mechanically work-hardening a ductile surface by repeatedly striking it with hard balls, usually entrained in a high velocity gas stream.

Shot peening (postdeposition processing)–Densifying a ductile film by repeatedly striking it with hard balls, usually entrained in a high velocity gas stream. Peening compacts the film and closes porosity.

Should–Term used in a specification or MPI that indicates a good practice but which is not mandatory. Example: gloves should be discarded after use. See *Shall, May*.

Shrinkage (sintering)–The reduction in volume due to firing.

Shutdown (vacuum technology)–Putting equipment in a safe and non-contaminating condition in preparation for non-use. Shutdown of a vacuum system may mean turning it off or may mean leaving the system under active high vacuum pumping.

Shutter (PVD technology)–A moveable optical baffle between the vaporization source and the substrate that prevents contaminants from the source from depositing on the substrate during the initial heating of the source. The shutter also minimizes radiant heating of the substrate before vaporization begins. The shutter can also be used to establish the deposition time.

Silicon carbide (abrasive)–Silicon carbide (SiC).

Siemens–A unit of conductance equal to the reciprocal of the resistance in ohms. See *Mho*.

Silica (substrate)–Silicon dioxide (SiO_2). Usually in the form of a glass called fused silica or fused quartz. The crystalline material called quartz.

Silicone oil (vacuum technology)–A heavy, low-vapor-pressure silicone-based (rather than hydrocarbon-based) oil that is commonly used in diffusion pumps and is sometimes used as a lubricant in vacuum systems. In diffusion pumps silicon oils are preferable to hydrocarbon oils since they are less prone to oxidation.

Silvering (chemical solution)–The deposition of silver from a solution by a catalyzed reduction reaction on the surface. Used to coat surfaces for mirrors and vacuum insulation. Example: vacuum-insulated flasks (Dewar flasks).

Single-unit processing (PVD technology)–Processing one (or a small number of) units at a time in contrast to processing a number of units each cycle (batch coating). Example: processing compact discs one-at-a-time with a cycle time of less than 3 seconds.

Sintering–To bond particles together by solid state diffusion to the contact points at an elevated temperature and sometimes under pressure. In many cases a small amount of bonding fluid may be present such as in glass-bonded "sintered" alumina. See *Hot Isostatic Pressing (HIP).*

Sizing (cleaning)–The lubricant applied to a thread to aid in weaving it into cloth. The sizing agent is often polyethyene glycol which is water soluble and can be removed by multiple washing. Sodium silicate also is used as a sizing agent but it is difficult to remove by washing.

Skim (cleaning)–To mechanically remove material that is floating on top of a fluid. Example: oil on water. See *Oleophillic filters.*

Skin (sintered material, sputtering target)–The dense surface layer that is sometimes formed on sintered materials.

Skull (evaporation)–The solid liner that forms between a molten material and a surface. The skull may be due to cooling such as a molten material in contact with a water-cooled copper hearth or may be due to the formation of a reaction layer such as molten titanium in contact with a carbon liner giving a TiC skull.

Slip agents (web coating)–Agents added to polymer films to increase the friction of the surface. Slip agents may be inorganic particles added to the film material or may involve chemical surface treatment.

Slip-cast–A suspension of particles (the Slip) that is formed into a shape, such as a plate or ribbon, before solidification. The solidified slip is then fired to drive off volatile materials and bond the particles together by fusion and/or sintering. Example: slip-cast alumina.

Slitting (web)–Cutting the web in the machine-direction to trim the web to create a more narrow web.

Slurry polishing–Polishing of a surface by particles in a fluid suspension (slurry) passing over a surface. If the slurry is very dilute the polishing may be called water polishing.

Smut (cleaning)–Residue of very fine particles on a surface after chemical etching or preferential sputtering. The particles are of second-phase material which are not attacked by the etchant. Example: copper smut left after etching an Al-2%Cu alloy with NaOH.

Snell's Law–The index of refraction of a material is the ratio of the sine of the angle of incidence of the radiation on a surface (from vacuum) to the sine of the angle of refraction in the material. See *Index of refraction.*

Snow (cleaning)–Solid material formed from a gas or fluid, usually by expansion and cooling (e.g., CO_2) used to clean a surface.

Soak (cleaning)–To leave in a fluid for a long period of time.

Soak (heating)–To leave at a high temperature for a long period of time.

Soak cleaning–See *Immersion cleaning*.

Soap (cleaning)–The water-soluble reaction product of a fatty acid ester and an alkali, usually sodium hydroxide. Used to emulsify oil contaminants.

Solder alloy–A metallic material that melts at a temperature less than 450°C and is used to join two materials together. See *Solder, tin-lead; Braze alloy*.

Solder, tin-lead (vacuum technology)–A solder alloy that contains tin and lead (63/37, 60/40) and does not contain any volatile constituents such as zinc or cadmium. It is thus suitable for use in a vacuum system.

Solids content–The amount of solid material left after the solvents have been volatilized. An important property of material deposited by flow coating such as basecoat material.

Solute–The material which goes into solution.

Solvent (cleaning)–A material capable of dissolving or taking into solution another material.

Soft water (cleaning)–Water that is free of ions, such as calcium and magnesium, that can form water-insoluble precipitates and residues. Soft water is produced by exchanging the ions with sodium and chlorine ions from NaCl. Sometimes used in rinsing before the final rinse which should be done using pure or ultrapure water. See *Water*.

Soft wall clean area (cleaning)–A clean area defined by hanging PVC plastic drapes where the filtered air flows from the ceiling downward and out under the drapes. The drapes may be in the form of strips (strip curtains).

Sol gel coating–The coating of a surface with a fluid sol which is a stable suspension of colloidal particles. The sol is then converted into a rigid porous mass called a gel, which is heated to melt and sinter the mass into a solid thin film.

Solid lubricant (vacuum technology)–A nonliquid material that provides lubrication and does not creep away from the point of application the way a liquid lubricant does.

Solid lubricant, low-shear metals–A solid lubricant used in high-torque application where lubrication is provided by deformation and shear of a non-workhardening metal. Example: silver and lead.

Solid lubricants, low-shear compounds–A solid lubricant used in low-torque applications where the lubrication is provided by shear between crystallographic planes. Example: MoS_2.

Solubility parameter (cleaning)–The amount of a specific material that a unit volume of a solvent will take into solution. Used to compare the relative cleaning power of cleaning solutions.

Solvent (cleaning)–Any substance that can dissolve another substance (the solute).

Sonoluminesce (cleaning)–The ultrashort bursts of light emitted by bubbles collapsing in a fluid.

Soot (CVD, reactive deposition)–Ultrafine particles formed by gas phase decomposition (CVD) and nucleation. See *Ultrafine particles*.

Sorption–The taking up of a gas by a solid or liquid material (sorbant) either by adsorption or absorption.

Sorption pump–Vacuum pump that operates by sorption of gases and vapors on surfaces which are usually cold. See *Vacuum pump*.

Sour cleaning bath (cleaning)–A chlorinated solvent bath that has become acidic by reaction with water to form HCl.

Space charge–The net charge in a volume of space caused by an excess of one charged species over another. Example: an excess of electrons and negative ions over positive ions will result in a negative space charge.

Spare parts (vacuum technology)–Spare parts to replace parts which, if they fail, will prevent use of the equipment. Also called *operational spares* (preferred). Example: spare roughing pump, spare o-rings.

Sparger (cleaning, electroplating)–Perforated pipe distributor for fluids or gases used in the bottom of fluid tanks for agitation.

Spark discharge plating–The transfer of material from a cathodic electrode to the anodic substrate in a periodic low-voltage, high-current arc in air or an inert gas.

Specific cleaning (cleaning)–Cleaning procedures directed toward removing specific contaminants. Example: removal of hydrocarbon contaminants by oxidation. See *Gross cleaning*.

Specific gravity (sg) (cleaning)–The ratio of the density of a material to the density of water, at a specific temperature.

Specific gravity (solution strength)–A method of specifying solution strength. Example: sulfuric acid varies from a sg of 1.0051 for a 1% aqueous solution (10.05 g/l) to 1.8305 for a 100% (1831 g/l) solution. See *Chemical solution, strength of*.

Specific heat–The quantity of heat needed to raise the temperature of a unit amount of material one degree.

Specification, process–The formal document which contains the "recipe" for a process and which defines the materials to be used, how the process is to be performed, the parameter windows and other important information related to safety, etc. Information on all critical aspects on the process flow sheet should be covered by specifications. See *Process flow sheet*.

Spectrophotometer–An instrument that measures radiation intensity at a specific frequency and over a broad band of frequencies.

Specular reflection, optical–Reflection at a specific angle determined by the angle-of-incidence of the incident beam. See *Diffuse reflection*.

Speed–The rate of change of position. Speed is a Scalar quantity. Example: miles-per-hour, feet-per-second. See *Velocity*.

Speed, pump–The volumetric rate of gas flow through a pump as measured in liters per second, ft^3/min, m^3/hr, etc. In order to obtain the mass flow rate (Torr-liters per second) the pressure must be specified.

Spin coating (semiconductor manufacturing)–Coating of a rapidly rotating surface with a fluid by applying the fluid at the center of the axis of rotation and letting centrifugal force carry the fluid to the edges where the excess is flung-off.

Spin dry (cleaning)–Removing most of the fluid from a surface by spinning at a high rate so that centrifugal force carries the fluid to the edge where most of the fluid is flung-off.

Spinning rotor gauge (vacuum technology)–A type of viscosity vacuum gauge that measures the deceleration of a levitated ball due to frictional drag with the gases present. Gauge output depends on the composition of the gases present.

Spit (evaporation)–A molten droplet of the evaporant ejected from the molten surface. Spits generally result from vapor bubbles rising through the molten material. See *Boiling beads*.

Splat cooling (thermal spray coating)–The rapid cooling of a molten droplet of material.

Split flow (leak detection)–When part of the helium flow passes through the leak detector and part through the high vacuum pumping system. See *Full flow*.

Sport (statistics)–Data point, event or product that occurs outside the norm for no obvious reason. Often disregarded in statistical analysis.

Spot cleaning (cleaning)–Cleaning of a localized area on the substrate.

Spray (cleaning, rinsing)–Spraying (in air) with an agent such as a solvent at a low pressure (100 psi) or a high pressure (1000 psi). Note: Some people use the term spraying to describe the use of high velocity fluid jets in the fluid of a cleaning tank. I would call this fluid jet agitation.

Spray rinsing (cleaning)–Spraying with soft or ultrapure water to rinse the surface.

Sputter cleaning (cleaning)–Removal of surface material in the deposition chamber by physical sputtering. See *In situ cleaning*.

Sputter deposition (PVD technology)–A physical vapor deposition process in which the source of the depositing atoms is a surface (target) being sputtered.

Sputter texturing–Surface roughening by preferential sputtering of crystallographic planes or due to isolated inclusions or patches of low-sputtering-yield material on the surface. See *Cone formation*.

Sputter-ion pump–A capture (getter) pump in which the gettering material is continuously being renewed by sputter deposition. See *Vacuum pump*.

Sputtered (as in sputtered films)–Poor terminology, it is better to use sputter deposited films.

Sputtering, Alternating Current (AC)–When two sputtering targets are electrically connected with each other such that when one target is the cathode the other is the anode with the polarity switching at a frequency of less than 50 kHz so each target is acting in a DC diode mode. This arrangement reduces the problems of the "disappearing anode effect" when reactively depositing insulating film.

Sputtering, chemical–The vaporization of surface atoms by chemical reaction with a reactive bombarding species resulting in an easily volatilized compound species. Example: sputter etching of silicon using bombardment with chlorine ions. See *Reactive plasma etching (RPE), Reactive ion etching (RIE)*.

Sputtering, physical–The physical ejection (vaporization) of a surface atom by momentum transfer in the near-surface region by means of a collision cascade resulting from bombardment by an energetic atomic-sized particle.

Sputtering, pulsed DC–A diode configuration in which the negative potential is applied as a fast rise-time DC pulse with a zero or reverse potential for a short portion of each cycle. The negative pulse time can be 60 to 90 % of the cycle time.

Sputtering configuration–The geometry used for sputtering. See *Magnetron, Deposition systems, Fixturing*.

Sputtering configuration, conformal target–When the sputtering target is conformal with the substrate geometry. Example: hemispherical target sputtering onto a hemispherical surface. See *Fixtures*.

Sputtering configuration, moveable target–A sputtering configuration where the sputtering target is moved while the substrate remains stationary. Used when coating very large substrates.

Sputtering configuration, opposing targets–When two or more (multiple of twos) planar unbalanced magnetrons face each other and the substrate is passed between the targets. The magnetic fields of the targets are such that the escaping magnetic field lines go from one target to another.

Sputtering efficiency (energy)–The amount of energy that is represented by the ejected sputtered atom (vaporization energy plus kinetic energy) to the amount of energy put into the surface by the bombarding species. Sputtering has a very low energy efficiency compared to thermal evaporation.

Sputtering target (PVD technology)–The material to be sputtered. Generally a cathodic surface in a gas discharge. See *Target*.

Sputtering threshold–The minimum incident particle energy necessary to cause sputtering.

Sputtering yield–The ratio of the number of atoms ejected to the number of high energy incident ions in the sputtering process.

Stabilizers (cleaning)–Materials added to chemicals such as solvents and oxidants to reduce the decomposition rate.

Staging ratio (vacuum technology)–Ratio of the pumping speed of one pump (or stage) to the next pump (or stage) in a multistage pump or train of pumps.

Stainless steel, austenitic (vacuum technology)–A non-magnetic, non-dispersion-hardenable stainless steel composed mainly of austenite (gamma iron with carbon in solution) stabilized by nickel. See *Stainless steel, martinsitic*.

Stainless steel, low carbon (vacuum technology)–A type of stainless steel, having a low carbon content used in situations where welding can cause precipitation of a carbide phase that can result in galvanic corrosion problems. Example: 304L and 316L stainless steel where the L designates a low-carbon content.

Stainless steel, martinsitic (vacuum technology)–A magnetic, dispersion-hardenable stainless steel mostly composed of martensite. See *Stainless steel, austenitic*.

Standard atmosphere–Atmospheric conditions of 760 Torr pressure and 0°C temperature.

Standard temperature (SEMI Standards)–Sometimes means room temperature i.e., 21°C ± 6°C (70°F ± 10°F).

Standard Temperature and Pressure (STP) conditions–Conditions of 760 Torr and 0°C.

Static electricity (cleaning)–The electric charge that is built-up on an insulator surface typically by friction and the charge separation associated with the friction. The amount of charge buildup depends on the conductivity of the surfaces and the humidity. Static charge buildup can be a problem with blow-drying insulating surfaces with un-ionized air.

Static dissipative material–Electrically conductive material that prevents static charge buildup. Example: electrically conductive gloves, conductive containers.

Static fatigue (adhesion)–The progressive loss of strength of a brittle material under tensile stress due to the weakening of the crack tip by water molecules.

Statistical design (experiments)–A technique of optimizing the information that is obtained from the least number of experiments. Useful for establishing process parameter limits. Also called *factorial design.* See *Parameter windows*.

Statistical Process Control (SPC) (manufacturing)–A method of measuring the variations in a processing step to help identify the cause of the variations.

Steam-jet pump (vacuum technology)–A kinetic vacuum pump where the gases are entrained in a jet of steam. Useful when there is a lot of particulate matter in the gas to be pumped. See *Water jet pump.*

Steered arc (plasma technology)–A cathodic arc where the arc is moved over the surface under the influence of a magnetic field. See *Random arc*.

Sterling (silver)–Silver with a purity of 0.925 fineness.

Sticking coefficient (film formation)–The ratio of the particles that remain on the surface to those striking the surface. Also called *sticking probability*.

Stitching, interfacial (adhesion)–Ion implantation through the interface to improve adhesion by imparting energy to the atoms in the interfacial region by collision.

Stoichiometric compound–A compound material which has the correct atomic ratios for all lattice sites to be occupied for the specific phase of the material. e.g., CuO (1:1) or Cu_2O (2:1). See *Sub-stoichiometric.*

Stoichiometry–The numerical ratio of atoms in a compound.

Storage, active (cleaning)–Storage in an environment where contaminants are continually being removed. Example: an ultraviolet-ozone cabinet where hydrocarbons are continually being oxidized. See *Storage, passive*.

Storage, passive (cleaning)–Storage in an environment that has been cleaned but is not being cleaned while the substrate is in the storage environment. Example: cleaned glass container. See *Active storage*.

Stones (glass)–Second-phase inclusions in the glass which produce visually observable defects. See *Seeds*.

Strain-to-fracture–Elongation before fracture.

Strained-layer superlattice–An epitaxial thin film where the lattice spacing of the crystalline structure of the film material has been strained but not to the point of creating dislocations.

Stranski-Krastanov model (nucleation)–Nucleation on a surface which changes structure during the initial deposition.

Stress (adhesion)–A stimulus (mechanical, chemical, thermal, etc.) that tends to disrupt some feature or property of a film material, such as adhesion.

Stress, residual film (film formation)–The residual compressive or tensile stress in a film that results from the growth process, phase change during fabrication or from differences in the coefficient of thermal expansion of the film and substrate.

Stress corrosion–Chemical corrosion whose rate is enhanced by the presence of mechanical stress that is internal to the material or applied externally. See *Wedging.*

Stress tensor (adhesion)–The stress components of tension and shear that appear at the interface. If the material deforms or changes properties during the application of mechanical stress the stress tensor may change.

Stress voiding (metallization)–The generation of internal voids by the movement of atoms under a tensile stress.

Striations (plasma)–Visual bands in the plasma that are due to plasma instabilities.

Strike (electroplating)–A thin ((1 micron) electrodeposited film that is to be overlayed with other deposited materials. Also called a *flash*.

Stripe, conductor (electrical)–A thin film conductor line produced using masking or etching techniques.

Strippable coating (cleaning)–A liquid coating, such as a soap or liquid polymer, that is applied to a surface which solidifies into a film which protects the surface from recontamination during some stage of processing. The coating material is removed during the subsequent cleaning processing.

Strippable coating, solid (cleaning)–A liquid coating applied to a surface which solidifies into a flexible film and whose purpose is to protect the surface from recontamination during some stage of processing. The strippable coating can also be used to coat-over particles that are removed when the coating is removed. See *Tack tape*.

Stripping (cleaning)–The removal of a film, coating or reaction layer from a surface.

Structure Zone Model (SZM) (film formation)–A diagram showing the morphology of a deposited film as a function of some deposition parameter. Example: temperature for vacuum evaporation; gas pressure and temperature for sputter deposition. See *Movchin-Demchishin diagram, Thornton diagram*.

Styles of learning (manufacturing)–The way people learn. Some people are more receptive to visual information and some are more receptive to auditory information. To be most effective in transferring information both should be used. Important in operator training. See *Technology transfer*.

Styles of thinking (technology transfer)–The characteristic of the way that people think (synthesis, realist, idealist, analyst, pragmatist). An important consideration in communication during technology transfer. See *Technology transfer*.

Sub-stoichiometric compound–A compound that does not have the correct ratio of elements to have the most stable structure. Example: TiN_{1-x} or SiO_{2-x}. See *Stoichiometric.*

Sublimation (PVD technology)–Thermal vaporization from a solid surface. See *Evaporation*.

Sublimation pump (vacuum technology)–A capture (getter) pump in which the getter material is periodically renewed by sublimation from a solid source. Example: titanium sublimation pump. See *Vacuum pump.*

Sublimation source (vaporization)–A vaporization source for heating materials, such as chromium, that sublime rather than evaporate. The sublimation source can function best by ensuring good thermal contact between the heater and the solid. Example: electroplated chromium on a tungsten heater or by heating by radiation in an oven-like structure, or by direct e-beam heating of the surface of the solid.

Substrate (PVD technology)–Surface on which the film is being deposited. See *Real surface*.

Suck-back (vacuum technology)–When the mechanical pumps stop, air will suck-back from the exhaust side to the low-pressure side bringing with it oil contamination from the mechanical pump.

Suction–The action of pushing a material toward a region of lower pressure. Generally by generating a vacuum so as to cause atmospheric pressure to push material toward the vacuum. Generally the vacuum used is very rough such as a fraction of a psi. Example: sucking liquid through a straw.

Sump (cleaning)–The liquid reservoir into which condensed vapors drain. See *Degreaser*.

Superconductivity–The disappearance of electrical resistance in a material below a certain temperature (critical temperature).

Supercritical fluid (SCF) (cleaning)–A vapor that has been compressed to a pressure above its critical pressure and heated to above its critical temperature. In this condition the vapor and the liquid have indistinguishable properties.

Supersaturation–The unstable condition when the vapor pressure of a material is above the saturation vapor pressure. Condensation is initiated by introducing condensation nuclei.

Suppliers (manufacturing)–Organizations from outside the company that supply materials, piece-parts, equipment, etc. Also called *qualified suppliers* if some basic criteria must be met.

Surface–The boundary between two different phases such as solid-gas or liquid-gas. Typically considered to be the first atomic layer of the solid or liquid. See *Near-surface region, Altered region.*

Surface analysis, terms of–See *ASTM Standard E 673-86a "Definitions of Terms Relating to Surface Analysis."*

Surface energy–The energy associated with the non-symmetrical coordination of atoms in the surface. This energy determines the maximum size of a droplet, the maximum size of a void in a fluid, the wetting of a fluid on a surface, and the agglomeration of atoms on a surface. Measured in dyne/cm, ergs/cm^2, mJ/m^2.

Surface Engineering–Changing the properties of a surface to meet a specific requirement. This can be done by applying a film or coating to the surface to create a new surface (overlay coating) or by changing the properties of the existing surface (surface modification).

Surface enrichment–The enrichment of some component of the bulk composition in the surface region as compared to the bulk. This may be due to loss of some constituent from the surface region or the preferential diffusion of species from the bulk to the surface region. Example: chromium enrichment in the surface region of stainless steel.

Surface mobility (adatom, film formation)–The ability of a deposited atom (adatom) to move over the surface before it nucleates and becomes immobile.

Surface modification–Changing the chemical, physical, mechanical or morphological properties of a surface. Substrate material is present in the modified surface.

Surface, non-removable (vacuum technology)–The surface in a vacuum chamber that cannot be removed for cleaning. Example: chamber walls, feedthroughs, tooling.

Surface, removable (vacuum technology)–The surfaces in a vacuum chamber that can be removed for cleaning. Example: fixtures, liners, shields.

Surface roughness (substrate)–The measure of the roughness of a surface from a mean value. See *Roughness, surface (R_a).*

Surface segregation–Segregation of a material to the surface. Example: diffusion of chromium through gold metallization to the surface where it oxidizes. The surface acts as a "sink" for the chromium.

Surfactant (surface-active agent) (cleaning)–A compound that reduces the surface tension between two fluids or between a fluid and a solid.

Susceptor, rf heating–An electrically conductive material that can be heated by rf and it in turn can heat a material that is in contact with it. Carbon is often used as a susceptor material in PVD and CVD technology.

Synthesis Reactions (CVD)–Reactions involving two precursor species resulting in the deposition of a compound such as a metal carbide, oxide, nitride, etc.

Tack–A measure of the "stickiness" of a surface.

Tack pad, floor (contamination control)–A sticky (high tack) surface placed on the floor and used to clean contamination from the soles of shoes and shoe coverings.

Tacky tape (cleaning)–A sticky (high tack) surface used to clean particulates from surfaces without leaving a significant amount of residual chemicals. See *Strippable coating*.

Tape test (adhesion)–A go or no-go (pass or fail) comparative adhesion test in which an adhesive tape is applied to a film surface and then rapidly pulled from the surface. Usually the film is scored under the area of test so that the tape pulls on a free edge of the film. See *Adhesion tests*.

Target (sputtering)–The surface being sputtered. Usually at a cathodic potential with respect to a plasma. Targets can be formed by machining, rolling, melting, vacuum melting, sintering, CVD, and plasma spraying.

Target, conditioning–Removal of the surface contamination such as oxides and degassing the target material before the sputter deposition begins.

Target assembly, sputtering–The component of the sputter deposition system that contains the sputtering target, the target backing plate (if used) and the target cooling assembly. See *Backing plate, target*.

Target bonding (sputtering)–Joining the target to the backing plate with a high thermal conductivity bond. Bond can be inspected by thermal analysis or ultrasonic inspection. See *Backing plate.*

Target conditioning (sputtering)–Sputtering a target with a shutter closed or the substrates out of line-of-sight, to remove natural contamination layers such as oxides from the target surface.

Target poisoning–Reaction of the surface of a sputtering target either with the reactive gas being used for reactive deposition or with a contaminant gas. The reacted layer causes a change in the performance of the sputtering target.

Target shielding (sputtering)–Shielding of the target to prevent establishing a plasma between the shield and the target. See *Paschen curve*.

Tear resistance (web)–Resistance to tear as measured by ASTM 1004.

Technological surfaces–See *Real surface.*

Technology transfer–The transfer of a product design and fabrication technology from Research and Development (R&D) into Manufacturing. This includes issues dealing with manufacturability and scale-up as well as the ability of individuals to communicate with each other both through written (formal) documents such as specifications and through informal and formal personal interactions (e.g., meetings).

Temperature–A measure of the average kinetic energy of particles in a material. It is important in communication between individuals that each person knows in what temperature units the other is using since normally the units are not specified. Example: "the substrate is heated to 100 degrees" (C or F?).

Temperature scale, Fahrenheit (°F)–The temperature scale based on the freezing point of water being 32°F and the boiling point of water under standard pressure conditions being 212°F.

Temperature scale, Centigrade (°C)–The temperature scale in which the freezing point of water is 0°C and the boiling point of water, under standard conditions, is 100°C. The degree centigrade has the same value as the degree Kelvin. Also called the *Celsius temperature scale*.

Temperature scale, Kelvin (K)–The temperature scale where zero is the point of no atomic or molecular motion and the heat content of a material is zero. The Kelvin degree has the same magnitude as the centigrade degree. Absolute zero is 0 K and -273.15°C.

Temperature Coefficient of Resistance (TCR)–The rate of change of resistance with temperature. The change is positive for metals and negative for insulators and semiconductors.

Tempered (fully tempered) glass–Glass that has a high compressive stress on the surfaces and a high tensile stress at the midplane. When fractured, the tempered glass breaks up into small shards. Also called *Toughened glass.*

Tempering (glass)—To place the surface of the glass in compression by heating above the strain point and then quenching the surface region before the interior has a chance to cool, thus giving a higher fracture strength. See *Tempered glass.*

Tempering (metal)—Heating briefly at a high temperature or heating at a low temperature to begin precipation hardening and thereby creating a tougher material.

Tensile stress (thin film) (PVD technology)–A stress resulting in the atoms being further apart than they would be in a non-stressed condition. The tensile stress tries to make the film material contract in the plane of the film.

Terpene (cleaning)–A natural homocyclic hydrocarbon solvent derived from plant life. Includes limonene which is derived from citrus fruit and pinene which is derived from pine trees. Example: turpentine.

Tesla (T)–The SI unit of magnetic field density equal to 1 Weber/m^2. See *Gauss*.

Testing-to-a-limit (adhesion)–Testing to a defined stress level. If the film does not fail it may be used as product. Example: wire-pull test to a given load. See *Adhesion.*

Texture (crystalline)–The preferential crystallographic orientation in a crystalline structure.

Texture (surface)–The roughness, wave pattern or other periodic morphological feature that describes a surface. See *Orange peel, Capillary waviness*.

Thermocouple–A temperature measuring device consisting of two dissimilar metals joined together such that the voltage generated across the junction is dependent on the temperature of the junction.

Thermal control coating (window)–A coating on windows that is used to reflect heat back into a room or keep out of a room.

Thermal decomposition (CVD)–The framentation of a molecule by heat alone.

Thermal desorption spectrum–The species and amount of material desorbed as a function of temperature. This spectrum indicates how well the species is bonded in the solid.

Thermal Gravimetric Analysis (TGA)–Chemical analysis by weight change as a function of temperature.

Thermal ionization–Ionization in a high-temperature combustion flame. Also called *flame ionization*.

Thermal oxidation–Formation of an oxide surface layer by heating a surface in oxygen. Example: formation of a passive oxide on stainless steel by heating to 450°C in very dry (-100°C dew point) air, oxidation of a clean silicon surface by Rapid Thermal Processing.

Thermal spray processes–A coating processes where material is melted by a plasma, electric arc or some other means and the molten particles are propelled to the substrate surface in a high velocity gas stream where they are splat cooled at a high quench rate.

Thermal stress adhesion test (adhesion)–Subjecting a coating-substrate structure to an elevated temperature to introduce stress due to the differences in thermal coefficient of expansions of the materials. The stress may cause failure or may introduce flaws that cause failure in subsequent testing. See *Adhesion tests*.

Thermal strengthening–Strengthening a high coefficient of expansion, low-thermal conductivity material, such as glass, by putting the surface in compression by heating the material to above its strain point then rapidly cooling the surface to below the strain point so that when the interior cools it is placed in tension. This puts the surface region into compression.

Thermal vaporization (PVD technology)–The vaporization of a material by raising its temperature. A useful vaporization rate for PVD processing is when the equilibrium vapor pressure is above about 2 mTorr. See *Evaporation, Sublimation*.

Thermalization (vacuum technology)–The reduction of the energy of an energetic particle to the energy of the ambient particles by collision, as it passes through the ambient.

Thermionic emission–See *Thermoelectronic emission*. Electron emission from a heated surface. This term is a misnomer since generally few ions are emitted from a heated surface for most materials. Exceptions are fluorine, cesium, potassium and rubidium which can be ionized by evaporation from a heated surface.

Thermistor gauge (vacuum technology)–A form of the Pirani gauge in which the resistor element is a semiconductor material rather than a metal.

Thermocompression (TC) bonding–The bonding of two surfaces under pressure and heat. Example: thermocompression wire bonding of a wire to a metallized surface. See *Ultrasonic bonding*.

Thermocouple gauge (vacuum technology)–A vacuum gauge that measures gas density by the cooling effect on a heated filament. See *Vacuum gauge*.

Thermoelectronic emission–Electron emission from a heated surface.

Thick film (PVD Technology)–A thick (> 1.0 microns) film deposited by PVD (or CVD) processing.

Thick film (hybrid microcircuits)–A conductive or insulating coating prepared by painting, screen printing or dip coating a slurry onto a surface followed by high temperature firing to remove binders and fuse the material to the surface. Thick films can be used to form conductive, resistive or insulating layers or patterns. Patterns can be applied by Screen printing.

Thickness, geometrical (film characterization)–The film thickness as measured in units of length. Examples: microns, angstroms, mils, nanometers.

Thickness, mass (film characterization)–The film thickness as measured by mass per unit area. Example: micrograms per square centimeter ($\mu g\text{-}cm^{-2}$).

Thickness, property (film characterization)–The thickness measured by some property of the film such as optical adsorption.

Thickness, optical (optical)–The geometrical thickness multiplied by the index of refraction.

Thin film (PVD technology)–There is no universally accepted definition of the term "thin film." Generally the term is applied to deposits having a thickness of less than several microns. The term can be used to describe surface layers that affect the optical, electrical or chemical properties of a surface and in some cases the thin film affects the physical and mechanical properties of a surface such as the abrasion resistance. Also called a *strike* in electroplating. See *Coating, Thick film*.

Threshold Limit Values (TLV) (safety)–The maximum amount of a chemical that a worker can be exposed to continuously or as a time-weighted-average (TWA) as defined by OSHA. Example: trichloroethylene 270 mg/m^3, arsine 0.05 mg/m^3, chlorine 1 mg/m^3.

Throttling (vacuum technology)–Reducing the conductance of vacuum plumbing by reducing the crossectional area by use of a valve or an orifice.

Throughput, mass (vacuum technology)–The amount of gas measured in pressure-volume units (Torr-liters) flowing through the pump or the system per unit of time.

Throughput, product–The number of units per hour that are completely processed.

Throwing power (electroplating, PVD technology)–The ability of a deposition process to cover a rough surface or deposit material in high aspect ratio (depth-to-width) surface features such as vias.

Time-Weighted Average (TWA) (safety)–The amount of material in the air to which a worker can be exposed during an 8-hour shift (OSHA). See *Permissible Exposure Limits (PEL) and Short Term Exposure Limits (STEL)*.

Tool (semiconductor processing)–System for performing a process (e.g. sputtering tool). Used synonymously with equipment.

Tool, wear-life of–How long a tool will perform satisfactorily. Measured as some tool function such as holes drilled, cut length, etc., under specified conditions.

Tooling–There is no universally accepted definition of the term "tooling" but it can be defined as the mechanical structure(s) in the deposition chamber that holds and moves the fixtures, vaporization source, shutters, masks, etc. Generally tooling is a non-removable structure in the system.

Tooling factor–The ratio of the observed condition, using sensors, during processing to the measured condition after processing. Example: ratio of the film thickness on a quartz crystal monitor, to the measured thickness of the film deposited on the substrate.

Topcoat (PVD technology)–A film or coating that is put on a deposited film structure, generally by a separate process. Example: lacquer coating on a deposited gold film to provide abrasion resistance.

Torr (or torr)–A unit of pressure defined as 1/760 of a standard atmosphere. See *Pressure, units of.*

Total film stress–The total stress developed by the sum of the incremental residual film stresses in the film. Total film stress is a function of the film thickness. See *Residual film stress*.

Total Life Cost (equipment)–The installed cost plus the cost of operating and maintaining the equipment through its lifetime. See *Installed cost, Cost-of-Ownership (COO).*

Total pressure–The sum of all the partial pressures of gases and vapors. See *Dalton's Law of Partial Pressures*.

Total pressure gauge–A vacuum gauge that measures the pressure effect of all gaseous and vapor species.

Toughness, fracture (adhesion)–The ability of a material to absorb energy and deform plastically before fracturing.

Toxic (chemical)–A chemical that has been shown to be toxic to mice. See *Carcinogenic, Mutagenic.*

Trace impurity–An impurity that occurs in a very small amount. Often in parts-per-million or parts-per-billion. See *Minor impurity*.

Trade-offs, design–Details of the design of a vacuum system that differ from the optimum vacuum design that are made to accommodate the use of the system in manufacturing. Example: large door openings to allow fixtures to be placed in the system, side-pumped chambers to prevent items from falling into the pumping system as can happen in a base-pumped system.

Trademark (™)–A letter, symbol, design, sound, etc., that has been registered with the US Patent and Trademark Office and is used to establish an identity to a product or producer.

Tradename (™)–An name given to a product or process to establish an identity for the product or process. Example: C-Mag™ and Meta-Mode™ for PVD processing equipment; Viton™ and Nichrome™ for materials.

Training–Instruction of an operator in the proper procedures and techniques as defined by the Manufacturing Process Instructions (MPIs).

Training, formal (manufacturing)–Training in a classroom by experienced instructors. See *On-floor training*.

Training, on-floor (manufacturing)–Training of an operator by having him/her work with an operator experienced in the process. Sometimes this is dangerous since bad habits can be passed from one to another. See *Formal training*.

Tramp elements (electroplating)–Undesirable ions in the electrolytic bath. See *Dummying*.

Transition flow (vacuum technology)–Gas flow conditions intermediate between viscous flow and molecular flow where the flow characteristics are determined by molecular collisions and collisions with the walls of the duct. Also called *Knudsen flow*.

Transmission Electron Microscopy (TEM)–An analytical technique which uses the scattering or diffraction of a high energy electron beam as it passes through a thin film to image the microstructure of the film. Scanning Transmission Microscopy (STEM) is used to analyze a surface area.

Transverse direction (web coating)–Direction normal to the direction that the web is moving. See *Machine direction*.

Trap (vacuum technology)–A device for stopping or impeding the flow of gases, vapors or particles through the system.

Traveler (manufacturing)–Archival document that accompanies each batch of substrates detailing when the batch was processed and the specifications and MPIs used for processing. The traveler also includes the Process sheet which details the process parameters of the deposition run.

Tribology–The science and technology of interacting surfaces in relative motion, and of associated subjects and practices such as lubrication.

Trigger arc (arc vaporization)–The high-voltage arc that is used to initiate the arc breakdown which is then sustained by the low-voltage, high-current arc.

Triode configuration (plasma)–A plasma configuration where a plasma is established between a cathode and an anode, often with magnetic confinement, and ions are extracted out of the plasma to a third electrode which is at a negative potential with respect to the plasma. Used in triode sputtering configurations.

Troy (t) weight scale–Weight scale used for weighing precious materials where 1 pennyweight (dwt) = 1.54 grams, 1 troy ounce = 20 dwt or 30.8 grams, 12 oz (t) = 1 lb (t). Conversion: one oz (a) = 0.913 oz (t) and one lb(a) = 1.22 lb (t). See *Avoirdupois weight scale*.

Tuning (plasma)–Matching the impedance of the load to that of the power supply so as to couple the maximum amount of energy into the load (plasma).

Turbomolecular pump (vacuum technology)–A compression-type vacuum pump with a series of stator (stationary) and rotor (moving) blades which impart a change in velocity to the gas molecules by their being struck by the high speed rotor blades and being reflected from the stator blades. The compression ratio that can be developed through the pump depends on the nature of the gas being pumped. Also called a *turbo pump*. See *Vacuum pump*.

Turbulent flow–A viscous flow with turbulent mixing.

Ultimate pressure (vacuum technology)–The pressure in a system toward which the pumping curve seems to be approaching asymptotically under normal pumping and processing conditions. Value will never be reached and depends on the sources of gases in the system. See *Base pressure*.

Ultrafine particle (cleaning)–Particle having a diameter less that about 0.5 microns. Generally formed by vapor phase nucleation of vaporized material or the residue from the evaporation of an aerosol. See *Vapor phase nucleation, Gas evaporation, Nanophase materials*.

Ultrahigh vacuum (UHV) (vacuum technology)–The vacuum region where the pressure is less than about 10^{-8} Torr.

Ultrapure water (UPW) (cleaning)–Water containing very low levels of ions, organic, particulate and biological contamination. Specifications can be as stringent as: resistivity is 18 megohm-cm continuous at 25°C; particle count is less than 500 particles (0.5 microns or larger) per liter; bacteria count is less than one colony (cultured for 48 hours) per cc; and organics are less than one part per million (ppm). See *Water*.

Ultrasonic agitation (cleaning, electroplating)–Agitation of a fluid, particularly in the boundary layer region, due to the formation and collapse of cavitation bubbles.

Ultrasonic bonding–Bonding under pressure and ultrasonic "scrubbing". Example: ultrasonic wire bonding to a film.

Ultrasonic cleaning (cleaning)–Cleaning due to the jetting action of the collapse of cavitation bubbles in contact with a surface.

Ultraviolet (UV) radiation–Electromagnetic radiation having a wavelength in the range of 0.004 to 0.4 microns. The short wavelength UV overlaps the long wavelength X-ray radiation and the long wavelengths approach the visible region.

Unbalanced magnetron (sputtering)–A magnetron configuration in which the magnetic fields are arranged so as to allow some of the secondary electrons to escape from the vicinity of the cathode to establish a plasma between the target and the substrate. See *Magnetron*.

Undercuring (polymer)–When a polymer resin has not been fully cured thereby leaving a large quantity of low molecular weight constituents in the polymer.

Underfiring, ceramic–When a sintered ceramic is not fired at a high enough temperature for a long enough time producing a weak, porous, easily fractured material.

Unplasticized polyvinyl chloride (uPVC)–Polyvinyl chloride (PVC) that does not contain plasticizers that can migrate to the surface and become a source of contamination. Tubing of the material is used to distribute ultrapure water. Also used as a material in contact with a clean surface.

Uptime (vacuum technology)–The percentage of time in which the equipment is in condition to perform its intended function. See *Downtime*.

UV curable (polymer)–Polymer basecoat material that can be cured by exposure to ultraviolet radiation, thus avoiding the problems associated with heat-curable polymers.

UV/Ozone (UV/O_3) cleaning–An oxidative cleaning process using ozone produced by ultraviolet radiation.

UV stabilizers–Chemical species added to polymers to adsorb the UV radiation and reduce decomposition of the polymer molecules by ultraviolet radiation.

Vacuum cadmium plating–Vacuum deposition of cadmium on high strength steel to avoid hydrogen embrittlement which can occur in electroplated cadmium. Also used to avoid water pollution problems. Also called *vac cad plating.*

Vacancy, lattice (crystallography)–A missing atom at a lattice site.

Vacuum–Pressure in a container that is less than the ambient pressure.

Vacuum, high–A gas pressure where there is molecular flow and a long mean free path for gas phase collisions. Generally taken as a pressure below about 10^{-5} Torr.

Vacuum, rough–Pressure from atmospheric to about 50 mTorr. See *Roughing.*

Vacuum, medium–The pressure range between rough vacuum and high vacuum.

Vacuum, Ultrahigh (UHV)–The vacuum region where the pressure is less than about 10^{-8} Torr.

Vacuum, Extra UHV (XUHV)–The pressure region less than about 10^{-10} Torr.

Vacuum arc–An arc formed in a vacuum such that all of the ionized species originate from the arc electrodes. See *Gaseous arc*.

Vacuum chamber–The enclosure that is evacuated and which the processing is to be performed. See *Chamber, deposition.*

Vacuum compatible materials (vacuum technology)–Materials that do not change characteristics in a vacuum and do not introduce contaminants into the system.

Vacuum deposition (PVD technology)–Films deposited by thermal vaporization of a material in a vacuum so that particles that leave the source do not collide with gas molecules before they reach the substrate. Often used synonymously with vacuum evaporation.

Vacuum engineering–The design and construction of a vacuum system to meet processing requirements. This includes the design trade-offs that make the system more amenable to operation, cleaning and maintenance. See *Vacuum technology*.

Vacuum evaporation (PVD technology)–Thermal vaporization of a material in a vacuum so that particles that leave the source do not collide with gas molecules before they reach the substrate. Often used synonymously with *vacuum deposition*.

Vacuum gauge–A device for measuring gas pressures below the ambient atmospheric pressure. Often some property other than pressure is measured and related to the pressure by calibration.

Vacuum gauge, capacitance manometer gauge–A vacuum gauge that uses the deflection of a diaphragm, as measured by the changing capacitance (distance) between surfaces, as an indicator of the pressure differential across the diaphragm. The pressure on one side being a known value.

Vacuum gauge, ionization, cold cathode gauge–A vacuum gauge that uses ion current formed by electron-atom collisions as an indicator of the gas pressure (density). The electrons are formed as secondary electrons from ion bombardment.

Vacuum gauge, ionization, hot filament gauge–A vacuum gauge that uses ion current formed by electron-atom collisions as an indicator of the gas pressure (density). The electrons are emitted from a hot thermoelectron emitting filament.

Vacuum gauge, Pirani gauge–A vacuum gauge that uses the resistance of a heated resistor element, which changes due to gas cooling, in a wheatstone bridge arrangement, as an indicator of the gas pressure (density).

Vacuum gauge, thermocouple gauge–A vacuum gauge that uses the cooling of a heated thermocouple junction as an indicator of the gas pressure (density).

Vacuum gauge, viscosity gauge–A vacuum gauge that uses the surface drag (deceleration) between the gas and a high velocity surface to measure particle density. Example: spinning rotor gauge. Also called a *molecular drag gauge*.

Vacuum melting–The melting of a metal in a vacuum environment to control contamination and aid in eliminating gaseous materials from the melt.

Vacuum pump (vacuum technology)–A device for reducing the gas pressure in a container to less than the ambient gas pressure. The vacuum pump can operate by capturing and holding the gases or by compressing and expelling the gases.

Vacuum pump, cryopump–A capture-type pump that operates by condensation and/or adsorption on cold surfaces. Typically there are several stages of cold surfaces. Typically one of the stages will have a temperature below 120 K. See also *Cryosorption pump, Cryopanel*.

Vacuum pump, diaphragm pump–A compression-type vacuum pump that operates using a flexible diaphragm that changes the volume of the pumping chamber by mechanical motion. A very clean pump that can be exhausted to atmospheric pressure. Used to back a turbopump with a molecular drag stage.

Vacuum pump, diffusion pump (DP)–A compression-type vacuum pump that operates by the collision of heavy vapor molecules with the gas molecules to be pumped giving the gas molecules a preferential velocity toward the high pressure stages of the pump. Also called a *vapor jet pump.*

Vacuum pump, getter pump–A capture-type vacuum pump that operates by reaction of a surface with the gaseous species to form a non-volatile reaction product or by absorbing the gases into the bulk of the getter material. In reaction-type getter pumps the getter materials are often deposited by evaporation or sublimation. Adsorption-type getter pumps are sometimes called non-evaporative getter pumps. See *Sublimation pump, Ion pump, Getter*.

Vacuum pump, ion pump–A capture-type vacuum pump where a getter material is deposited by sputtering and gaseous ions are accelerated to the reactive surface to react with the surface or be physically buried in the depositing material. Also called a *getter ion pump*.

Vacuum pump, mechanical pump–A compression-type vacuum pump with moving parts. The term is generally applied to pumps used for roughing or backing (e.g. oil-sealed mechanical pump, piston pump, diaphragm pump, etc.), and not high vacuum pumps (e.g., turbomolecular pumps).

Vacuum pump, sorption pump–A capture-type vacuum pump that operates by cryocondensation of gases on a large-adsorption-area cryogenically cooled (< -150°C) surfaces.

Vacuum pump, sublimation pump–A getter pump where the getter material, such as titanium, is deposited by sublimation from a solid surface.

Vacuum pump, turbopump–A compression-type vacuum pump with an series of stator (stationary) and rotor (moving) blades which impart a change in velocity to the gas molecules by their being struck by the high speed rotor blades and being reflected from the stator blades. The compression ratio that can be developed through the pump depends on the nature of the gas being pumped.

Vacuum surface (vacuum technology)–A surface in contact with the vacuum environment.

Vacuum surface, removable–Surfaces, such as fixtures, that are routinely removed from the system or surfaces such as liners that can be removed from the system for cleaning.

Vacuum surface, non-removable–The surfaces, such as chamber walls, that are not easily removed and must be cleaned in place.

Vacuum technology (vacuum technology)–The operation, cleaning, maintenance and repair of a vacuum system so that it continues to meet processing requirements. See *Vacuum engineering*.

Vacuum-based ion plating (film deposition)–A special case of ion plating where the deposition is done in a high vacuum and the concurrent or periodic bombardment is provided by ions accelerated from an ion gun or plasma source. Also called *Ion Beam Assisted Deposition* (IBAD).

Valence–The number of excess charges (positive or negative) associated with an atom, molecule, or radical.

Valve (vacuum technology)–A mechanical device that can start, stop or regulate the flow of a gas or fluid by use of a moving part that opens or obstructs a passage.

Valve, angle–A valve that does not provide an optically straight path through the valve opening.

Valve, ballast (vacuum technology)–A valve to allow the admittance of a gas into the foreline or the inlet of the roughing pump to prevent condensation of vapors by compression and prevent suck-back. See *Suck-back*.

Valve, butterfly (vacuum technology)–A valve in a tube that operates by rotating a plate along an axis that is through the diameter of the tube.

Valve, check–A valve that limits flow to one direction only.

Valve, gate–A high-conductance valve that is sealed by a moving plate.

Valve, high vacuum–The valve between the high vacuum pump and the volume to be evacuated.

Valve, in-line–A valve that provides an optically straight path through the valve opening.

Valve, isolation–A valve that isolates one vacuum chamber from another. Often the pressures in the two chambers are nearly equal.

Valve, Normally Closed (NC)–A valve that is closed when there is no actuating force.

Valve, Normally Open (NO)–A valve that is open when there is no actuating force.

Valve, poppet–A mechanical vacuum sealing valve where the motion of the sealing plate is normal to the plane of the seal.

Valve, pneumatic–A valve that is actuated by air pressure.

Valve, pressure relief–A safety valve that opens when the pressure on the system-side exceeds some predetermined value.

Valve, roller–A valve used on a continuous sheet where rollers contact the surface above and below the sheet to give vacuum sealing.

Valve, roughing–The valve between the roughing pump and the volume to be evacuated.

Valve, slit–A mechanical sealing valve that has a long, narrow rectangular opening. Often used in passing flat and thin substrates, such as silicon wafers and architectural glass plates, into a chamber. Also called a *slot valve*.

Valve, soft-roughing–A valve whose variable conductance allows the system to be rough-pumped slowly to minimize turbulence in the system.

Valve, soft-vent–A valve whose variable conductance allows the system to be returned to ambient pressure slowly to minimize turbulence in the system.

Valve, solenoid–A valve that is actuated by an electromagnetic action.

Valve, throttling–A valve used to control the pumping speed. It may be special valve such as a variable conductance valve or it may be a standard on-off valve that is only closed part-way, possibly by hand.

Valve, variable conductance–A valve whose conductance can be varied in a controlled manner. Generally refers to large valve openings. Usually not designed to completely close-off the gas flow. See *Valve, variable leak*.

Valve, variable leak–A variable conductance valve that is designed to control a very small gas flow (leak) of a few to several hundred standard cubic centimeters per minute (sccm). Used as part of a mass flow controller. See *Mass flow controller*.

Valve, vent–Valve to allow the system to be returned to ambient pressure. See *Valve, soft-vent*.

Valve metals–Metals which can be oxidized to form dense, coherent oxide layers. Examples: aluminum, titanium and niobium.

Vapor–A gas that is easily condensed by cooling, compression, etc. The term gas is often used in a context that includes vapors. See *Gas*.

Vapor condensation (cleaning)–A solvent is heated to form a vapor cloud above the surface and a cold part is suspended in the vapor. The solvent condenses on the part and flows off into the "sump" carrying the contaminants with it. When the part is heated to the vapor temperature, condensation ceases and cleaning action stops. See *Degreaser, vapor*.

Vapor cleaning–Cleaning by the condensation of a solvent vapor on a cold surface above a hot liquid Sump. The condensed solvent and contamination flows off into the sump. Cleaning continues until the part reaches the temperature of the vapor and condensation ceases. Also called *vapor degreasing*.

Vapor dry (cleaning)–Drying by condensing a vapor on the surface that displaces the water and flows off into a "sump." Usually done hot so that the high vapor pressure drying agent is rapidly vaporized from the surface.

Vapor forming–Fabrication of a free standing structure by depositing material from a vapor onto a mandrel and then removing the mandrel.

Vapor jet pump (vacuum technology)–A kinetic pump where the gas molecules are entrained in a jet of fluid vapor. See *Diffusion pump, Venturi tube*.

Vapor lock–Interruption of fluid flow through a channel by the creation of a vapor bubble in the channel due to excessive heating.

Vapor Phase Epitaxy (VPE) (PVD technology)–Formation of single crystal films by Chemical Vapor Deposition (CVD) processes. See *Chemical Vapor Deposition (CVD)*.

Vapor phase etching (cleaning)–Chemical etching using a vapor instead of a fluid.

Vapor phase nucleation–The development (condensation) of nuclei in the gas phase due to multi-body collisions. See *Ultrafine particles, Gas evaporation, Black sooty crap (BSC)*.

Vapor pressure, equilibrium–The pressure of the vapor of a solid or liquid above the surface in a closed container such that as many particles return to the surface as leave the surface. Also called the *saturation vapor pressure*.

Vapor pump, cryopanel–A capture-type vapor pump that removes vapors, by cryocondensation on large-area surfaces, often within the vacuum chamber, which are at temperatures of -100 to -150°C. At this temperature the vapor pressure of water is very low. Also called a *Meissner Trap*.

Vaporization (volatilization)–The conversion of a solid or liquid to a vapor by any means such as thermal, arcing, sputtering, etc.

Vapour–See *vapor* British spelling for vapor.

Velocity–A Vector quantity of motion that has both speed (a scalar not a vector quantity) and direction. Example: miles-per-hour to the north. Note: A change in direction is a change in velocity even when there is no change in speed.

Vented bolt (vacuum technology)–A bolt that has a hole down the axis or a groove through the threads to avoid forming a virtual leak when the bolt is inserted in a blind hole.

Venting (vacuum technology)–Bringing the system up to ambient pressure. See *Backfill*.

Venturi tube (vacuum technology)–A constriction in a pipe that causes an increase in the velocity of a fluid or gas and creates a vacuum that can be used to draw fluid or gas into the main flow of fluid or gas through a port in the constriction. Example: used in a carburetor to draw fuel into the air stream, used as a suction pump in a chemistry laboratory when placed on a water faucet.

Via (semiconductor processing)–A hole that extends from one level of a multi-layer structure, through an intermediate layer, usually an insulator, to another layer. To make electrical contact between layers the hole must be filled with a conductive material.

Vibration (vacuum technology)–Repetitive movement of surfaces (cm/s) which can contribute to particulate generation by wear and pinhole flaking. Origin of vibration may be the system location or from the mechanical pumping system.

Vicinal surface–A surface of a single crystal material that has been cut and polished at an angle to a crystallographic plane in order to give a "stepped-surface" on an atomic scale. Also called an *off-cut surface*.

Vickers hardness number–The expression derived from the force used and the projected area of an imprint obtained by an square shaped (ASTM E 348) diamond indenter forced into a surface. Abbreviated HV (formally VHN). HV = 1854.4 P/d^2 where P = grams force and d = length of diagonal in microns.

Virtual leak (vacuum technology)–A conduction path from an internal trapped volume to the main volume of a vacuum system (no connection to the outside ambient environment). Example: void below the bolt in a blind, tapped hole.

Viscous flow (vacuum technology)–Gas flow where the mean free path for collision is very small compared to the dimensions of the system. Flow may be laminar or turbulent.

Visible radiation–Electromagnetic radiation that is visible to the human eye. Electromagnetic radiation in the wavelength range of ~0.38 to 0.78 microns.

Vitreous (material)–A glassy (no discernible crystal structure) material. See *Crystalline*.

Void (film growth)–A region lacking solid matter. The void may be enclosed with no connection to a free surface or it can be connected to a free surface. Also called a *pore*.

Volatile organic compounds (VOCs) (cleaning)–Organic compounds, such as solvents, that have boiling points below 138ºC.

Volcanoes–Eruptions in a film where reactive gases or vapors have reacted with the underlying material to form corrosion products.

Volume flow rate (vacuum technology)–The volume of gas passing through a pump or system at a specific pressure and temperature. Measured in liters/sec. Also called *throughput*. See *Mass flow, Pumping speed*.

Wafer (semiconductor processing)–A specific type of substrate, usually a thin disk of silicon or GaAs.

Wall creep (vacuum technology)–Movement of an adsorbate along a surface.

Warm-up time (diffusion pump)–The time necessary to bring the pumping fluids in a diffusion pump up to the proper operating temperature.

Warm-up time (Mass flow meter)–Time for a mass flow meter to warm to operating temperature.

Water (H_2O) (cleaning)–Common cleaning solvent for ionic contaminants and as a rinsing agent. Often used as a water-alcohol mixture to lower the surface energy of the fluid.

Water, de-ionized (DI water)–Water with a low ionic content as measured by its electrical conductivity. Sometimes used synonymously (incorrectly) with pure water or ultrapure water. This is incorrect since DI water can still have organic and particulate contamination.

Water, distilled–Water purified by distillation often by several distillation stages (i.e., triply distilled water).

Water, hard–Water containing a high concentration of easily precipitated ions such as Ca, Mg, Fe.

Water, pure–Water purified by reverse osmosis (RO) along with carbon filtration (organics) and mechanical filtration (particulates). Often used as a solvent and as a rinsing agent where requirements allow.

Water, semiconductor grade–Water that is pure enough to meet the requirements of the semiconductor processing industry. See *Water, ultrapure.*

Water, soft–Water in which easily precipitated ions, such as Ca, Mg, Fe, have been replaced by more soluble ions such as Na. Often used as an intermediate rinsing agent.

Water, ultrapure–Water containing a very low concentration of materials (ionic, organic, inorganic, biological, etc) that will leave a residue on evaporation. Produced by ion exchange (ionic species), carbon filtration (organics), and mechanical filtration (particles, biological agents). The most pure rinsing material.

Water adsorption–Amount of water taken up by a material after a 24 hour immersion.

Water jet pump–A kinetic vacuum pump where the gases are entrained in a jet of water. See *Venturi tube*.

Water spot (cleaning)–The spot of residue left from the evaporation of impure water.

Water-break test (cleaning)–A test for hydrophobic contamination by observing the sheeting action of water on the surface. If the sheet of water avoids certain hydrophobic areas contamination is to be expected in those areas. See *Sheeting*.

Watt (W)–The SI unit of power.

Wavelength–The distance between two points having the same phase in two consecutive cycles of a periodic wave. Example: the wavelength of electromagnetic radiation.

Wavenumber–The reciprocal of the wavelength.

Weak-surface-layer (adhesion)–When the surface layer is weak either due to a low-molecular weight layer (polymer) or surface flaws (brittle solid). During film deposition this weak region becomes part of the interphase material resulting in poor apparent adhesion.

Wear–The removal of material by friction between material in moving contact.

Web (PVD technology)–A thin, flexible membrane that may be solid or perforated.

Web, polymer, properties of–Some properties of web materials are: surface energy, tear strength, puncture-resistance, impact strength, clarity, flexibility, heat-sealing characteristics, thermal stability, shrink-film performance.

Web coating (PVD technology)–Depositing a film on a web of material, usually of a polymer or paper. Aluminum is the most commonly deposited film material.

Wedging action (corrosion, adhesion)–When there is corrosion at an interface and the solid or gaseous corrosion product expand and exert a stress on the interface thus enhancing the corrosion rate and the loss of film adhesion.

Weight–A measure of the gravitational attraction of a body. Often used synonymously (but incorrectly) with mass. See *Mass*.

Weight-gain analysis (cleaning)–An analysis of the rate and amount of material absorbed by another material in a given environment. Example: this is of concern in recontamination where moisture pickup after bakeout will determine the storage environment needed.

Weight-loss analysis (cleaning)–The analysis of the desorption or extraction of material from the bulk as a function of the ambient environment. Example: desorption of water during vacuum baking will determine the time and temperature needed to desorb the water to an acceptable level.

Weld (fusion weld) (vacuum technology)–Joining two materials by melting and mixing the materials in the interfacial region. Care must be taken that flaws and stresses are not generated in the heat affected zone (HAZ) during cool-down.

Wetting agent (cleaning)–A chemical that reduces the surface energy of a fluid which makes it flow over a surface (wet) more easily. Example: Alcohol in water.

Wetting angle–The angle that a drop of liquid makes with a surface as measured through the liquid.

Wetting growth (film formation)–The lateral growth of nuclei on a surface due to the strong interaction of the adatoms with the surface. See *De-wetting growth.*

What-if game (vacuum technology)–The question and answer session used to establish a fail safe design by asking what will happen if something fails. Example: what happens if the power goes off for one minute? for an hour?

White metal–White-colored metals such as aluminum, magnesium, antimony and zinc and some of their alloys. Also called a *gray metal*.

White room–A clean area that uses many of the construction practices, equipment and techniques of a cleanroom but does not use high volumes of filtered air. See *Cleanroom*.

Window (vacuum technology)–A feedthrough that allows optical (optical window) or magnetic (magnetic window) radiation to pass through the chamber wall. See *Feedthrough*.

Window, process parameter–The region between the process parameter limits that allows a satisfactory product to be produced. The larger the window the more robust is the process. Example: 100°C ± 10°C.

Wipe clean (cleaning)–See *Wipe-down*.

Wipe-down (cleaning, vacuum technology)–Cleaning/drying a surface by wiping with a lint-free, compliant, low-extractable material, such as a cloth or sponge, which contains a cleaning/drying fluid such as anhydrous alcohol.

Wire bond–An electrical connection to a surface made by pressing a section of wire under heat and pressure (thermocompression bonding) or pressure and ultrasonic scrubbing (ultrasonic bonding) against the surface. See *Ball bond*.

Witness plate–A substrate that is not a part of the production batch but is used for characterizing some portion of the process or some film property such as film thickness, film stress, film adhesion, etc. Also called a *monitor plate*.

Work hardening–The hardening of a material by repeated deformation creating a lot of lattice dislocations. The hardening can be removed by annealing above the recrystallization temperature. Example: the knife-edge on a CF flange is hard because of work hardening of the stainless steel during machining. If the flange is heated to above 450°C the knife-edge will be ruined by annealing.

Work of adhesion (W_a), thermodynamic (adhesion)–The thermodynamic work-of-adhesion (W_a) between two polymer materials (1 and 2), in ideal contact, is given by the Dupre relation: $W_a = \delta_1 + \delta_2 - \delta_{1,2}$ Where δ_1 and δ_2 are the surface energies and $\delta_{1,2}$ is the interfacial energy.

X-ray–Short wavelength (≈1 Å) electromagnetic radiation.

X-ray diffraction–Diffraction, usually of crystalline lattices, using x-ray radiation.

X-ray emission–The generation of characteristic x-rays by bombarding a surface with high energy electrons.

X-ray Fluorescence (XRF) spectroscopy (characterization)–The generation of characteristic x-ray radiation from a surface by bombarding the surface with X-rays. The emitted characteristic X-rays are characterized by their wavelength or their energy. The analytical technique is a non-destructive technique for determining element composition of a layer up to several microns in thickness depending on the mass of the elements.

X-ray Fluorescence (XRF) spectroscopy, energy dispersive (ED-XRF) (characterization)–X-ray fluorescence analysis (X-rays as the probing species and X-rays as the detected species) where the detected species is energy analyzed in a lithium-drifted detector.

X-ray Fluorescence (XRF) spectroscopy, wavelength dispersive (WD-XRF) (characterization)–X-ray fluorescence analysis (X-rays as the probing species and X-rays as the detected species) where the detected species is analyzed as to its wavelength using a crystal diffractometer.

X-ray Photoelectron Spectroscopy (XPS) (characterization)–A surface analytical technique where the probing species are X-rays and the detected species are photoelectrons. The technique allows both species identification and the chemical bonding energy. See also *Electron Spectroscopy for Chemical Analysis*.

X-ray thickness measurement–Measurement of the thickness (mass per unit area) by the attenuation of X-rays passing through the material. See *Thickness*.

Xerography–Xerography is done by the attraction of electrically charged "toner" to a paper which has been charged by exposure to an optical image and then fusing the toner to the paper with heat. The charging drum is coated with selenium or other photosensitive material. Also called *electrography.*

Yield, product–The percentage of substrates that enter the production processing sequence that result in good product. See *Throughput, product.*

Yield, secondary electron–The number of electrons emitted from a surface per incident electron or incident ion. The secondary electron yield for electrons is much higher than for ions.

Yield, sputtering–The number of ejected (sputtered) surface atoms per incident high energy bombarding particle (ion).

Yield stress–The lowest stress at which a material will begin to plastically deform under mechanical stress.

Young's modulus–The ratio of the applied tensile stress to the resulting elastic strain.

Zeolite–A high surface area mineral that is a molecular sieve material used in sorption pumps and cryosorption traps. Must be regenerated at 200°C or more. See *Molecular sieves.*

Zeroing (a meter)–Moving the indicator point of a meter reading to a zero reading at zero input.

Zeta potential–The electrical potential that exists across the interface between a solid and liquid.

ACRONYMS

A–Ampere

Å–Angstrom

AAS–Atomic Adsorption Spectroscopy

ACGIH–American Conference of Governmental Industrial Hygienist

ACS–American Chemical Society

AEM–Analytical Electron Microscopy

AES–Auger Electron Spectroscopy

AESF–American Electroplaters and Surface Finishers

AFM–Atomic Force Microscopy, Abrasive Flow Machining

AIMCAL–Association of Industrial Metallizers, Coaters and Laminators, Inc.

AIP–American Institute of Physics.

AMLCD–Active-Matrix Liquid Crystal Display

AMR–Anisotropic MagnetoResistive

ANSI–American National Standards Institute

APCVD–Atmospheric Pressure CVD

APIMS–Atmospheric Pressure Ionization Mass Spectrometry

APS–American Physical Society.

AR–AntiReflecting

ARC–AntiReflective Coating

ARE–Activated Reactive Evaporation

ARIP–Activated Reactive Ion Plating

ASIC–Application Specific Integrated Circuit

ASM–ASM International (Previously American Society for Metals now ASM International)

ASME–American Society of Mechanical Engineers

ASNT–American Society for Nondestructive Testing

ASQC–American Society for Quality Control

ASTM–American Society for Testing and Materials

AVEM–Association of Vacuum Equipment Manufacturing

AVS–American Vacuum Society

a (α)–amorphous (Example: a-Si or α-Si)

amu–atomic mass unit

atm–atmosphere (usually standard atmosphere)

B–Magnetic field (vector)

BOPP–Biaxially oriented polypropylene.

BPSG–BoroPhosphoSilicate Glass

BRDF (light)–Bidirectional Reflectance Distribution Function

BSC–Black Sooty Crap

bcc (crystallography)–body centered cubic

bp–boiling point

C–Capacitance, Ceiling

CAD–Computer Aided Design

CAM–Computer Aided Manufacturing

CCAI–Chemical Coaters Association International

CCD–Charged-coupled Devices

CCW–Counter Clockwise

CD–Compact Disc, Critical Dimension

CDG–Capacitance Diaphragm Gauge

CDMS–Chlorodimethylsilane

CEVC–Completely Enclosed Vapor Cleaner

CF™–ConFlat (flange)

CFC–Chlorofluorocarbon

CFC-111–Trichloroethane

CFC-113–Trichlorotrifluoroethane

CGA–Compressed Gas Association

CIE–Commission International de l'Eclairage (International Comimssion on Illumination)

CLA–Center Line Average

CLEO–Conference on Laser and Electro-Optics

CMOS–Complementary metal-oxide semiconductor

CMP–Chemical-Mechanical Polishing, Chemical-Mechanical Planarization

CMM–Converting Machinery/Materials

CNDP–Cold Neutron Depth Profile

COO–Cost Of Ownership

CPP–Cast Polyproplylene

CrP–Chromium-rich oxide Passivation

CRT–Cathode Ray Tube

CTE–Coefficient of Thermal Expansion

CTMS–Chlorotrimethylsilane

C-V–Capacitance-Voltage

CVD–Chemical Vapor Deposition

CW–Clockwise

c–velocity of light in a vacuum

cc–cubic centimeter

cfm–cubic feet per minute

cfs–cubic feet per second

cgs–centimeter-gram-second (system of units)

cm–centimeter

DCS–Dichlorosilane

DI–Deionized water

Diff–Diffusion pump

DIW–Deionized Water

DLC–Diamond-Like-Carbon

DMS–Dual Magnetron Sputtering

DMSO–Dimethyl Sulfoxide

DOP–Dioctyl Phthalate

DOT–Department of Transportation

DP–Diffusion Pump

DRAM–Dynamic Random Access Memory

DTIC–Defense Technical Information Center

DUV–Deep UltraViolet

dwt–pennyweight

E–Electric field (vector), expodential

ECR–Electron Cyclotron Resonance

EDX–Energy Dispersive X-ray

ECS–Electrochemical Society

EDTA–Ethylene Diamine Tetraacetic Acid

ELD–Electroluminescent Display (flat panel)

EMI–Electromagnetic Interference

EPA–Environmental Protection Agency

Epi–Epitaxial

ERA–Evaporative Rate Analysis

ESCA–Electron Spectroscopy for Chemical Analysis

ESD–ElectroStatic Discharge

emf–electromotive force

epi–epitaxial

eV–electron volt

F–Farad

FDD–Floppy Disc Drive

FEC–Field Emission Cathode

FED–Field Emission Display, Field Emission Diode

FET–Field Effect Transistor

FLIR–Forward Looking InfraRed (7.5 to 12 (m)

FPD–Flat Panel Display

FT-IR–Fourier Transform–Infrared Analysis

fcc–face centered cubic

fpm–feet per minute

G–giga (suffix for 10^9), unit of magnetic field strength (gauss), gallons

GDMS–Glow Discharge Mass Stectrometry

GFSI–Ground Fault Circuit Interrupter

GPM–Gallons Per Minute

g–unit of gravitational acceleration, gram

gr–grain

H–Hour, Henry (unit of inductance)

HAP–Hazardous Air Pollutants

HAZ–Heat-affected zone, Hazardous (material)

HEED–High Energy Electron Diffraction

HEPA–High Efficiency Particle Air

HCD–Hollow Cathode Discharge

HCL–Hollow Cathode Lamp, hydrochloric acid

HDD–Hard Disk Drive

HDP-CVD–High Density Plasma–CVD

HF–Hydrofluoric acid

HFCVD–Hot Filament Chemical Vapor Deposition

HMC–Hybrid Micro Circuit

HMDSO–Hexamethyldisiloxane

HVOF–High Velocity Oxygen Fuel

HWOT–Half Wave Optical Thickness

Hz–Hertz (cycles per second)

h–Planck's constant

hcp–hexagonal close packed

IAD–Ion Assisted Deposition

IARC–International Agency for Research on Cancer (establishes carcinogenicy of materials).

IBA–Ion Beam Analysis

IBED–Ion Beam Enhanced Deposition

IC–Integrated Circuit

ICB–Ionized Cluster Beam (deposition)

ICP–Inductively Coupled Plasma

ICP-MS–Inductively Coupled Plasma Mass Spectrometer

ID–Internal Diameter

IDLH–Immediately Dangerous to Life or Health

IES–Institute of Environmental Sciences

IEEE–Institute of Electrical and Electronic Engineeers

ILD–InterLayer Dielectric

IMD–InterMetal Dielectric

IPA–IsoPropyl Alcohol

IPC–Institute for Interconnecting and Packaging Electronic Circuits

ISHM–International Society for Hybrid Microelectronics.

ISO–International Standards Organization

ISS–Ion Scattered Spectrometry

ITO–Indium-tin-oxide

IVD–Ion Vapor Deposition

J–Joule, electric current (vector)

JVST–Journal of Vacuum Science and Technology

K–dielectric constant, Karat (fineness of gold)

k–kilo (suffix for 10^3), Boltzman's constant, Portion of the complex index of refraction given by n-ik or n(1-ik), optical extinction coefficient ($k = \alpha\lambda/4$)

kcal–kilocalorie

kWH–kilo-watt-hour

L–Low (carbon steel), liter (preferred)

LASER–Light-amplification by Stimulated Emission of Radiation

LC_{50}–Median lethal dose

LCD–Liquid Crystal Display

LCM–Laser Confocal Microscope

LCVD–Laser Chemical Vapor Deposition

LDPE–Low Density Polyethylene

LED–Light Emitting Diode

LEED–Low Energy Electron Diffraction

LLDPE–Linear Low Density Polyethylene

LPCVD–Low Pressure Chemical Vapor Deposition. See also *SACVD.*

LPPS–Low Pressure Plasma Spray

LIMA–Laser-induced mass analysis

LLS–Linear Least Squares (statistical analysis)

LN and LN2–Liquid Nitrogen

LPCVD–Low Pressure Chemical Vapor Deposition

LTEL–Long Term Exposure Limits

LWP–Long Wavelength Pass filter

l–liter (not preferred)

M–mega (prefix for 10^6), Minute

MBE–Molecular Beam Epitaxy

MCrAlY–Metal-Chromium-Aluminum-Yitterium

MD–Movchan-Demchiskin, Machine Direction

Me–Metal

MEC–Methylene Chloride

MEMS–Microelectromechanical Systems

MFC–Mass Flow Controller

MFM–Mass Flow Meter

MFSA–Metal Finishing Supplier's Association

ML–Monolayer

MLAR–Multi-layer Antireflection Coating

MLS–Monolayers per Second

MMIC–Monolithic Microwave Integrated Circuits

MNS–Metal-nitride-silicon

MO–Magneto-Optical

MOCVD–Metal-organic Chemical Vapor Deposition

MOS–Metal-oxide Semiconductor

MPI–Manufacturing Process Instruction

MR–Magnetoresistive

MRS–Materials Research Society

MSDS–Materials Safety Data Sheet

MTR–Material Test Report

m–milli (suffix for 10^{-3})

mcg–micrograms

min–minute

mks–meter-kilogram-second

NACE–National Association of Corrosion Engineers

NAMF–National Association of Metal Finishers

NBS–National Bureau of Standards which has been renamed NIST.

NC–Normally closed

NDE–Non-Destructive Evaluation

NDT–Nondestructive Testing

NESHAP–National Emission Standards for Hazardous Air Pollutants

NIST–National Institute of Science and Technology (USA)

NO–Normally open

NREL–National Renewable Energy Laboratory

NVR–Non-Volatile Residues

n–Index of refraction, Portion of the complex index of refraction given by n-ik or n(1-ik)

nm–nanometer

OD–Optical Density, outside diameter

ODP–Ozone Depletion Potential

OEM–Original Equipment Manufacturer

OPP–Oriented Polypropylene

OSEE–Optically Stimulated Electron Emission

OSHA–Occupational Safety and Health Administration (USA)

OTR–Oxygen Transmission Rate

OVD–Optically Variable Device

QWOT–Quarter Wave Optical Thickness

OXTR–Oxygen Transmission Rate

oza or oz(a)–Avoirdupois ounce

ozt or oz(t)–Troy ounce

Pa–Pascal

PAPVD–Plasma Assisted Physical Vapor Deposition

PAVD–Plasma Assisted Vapor Deposition

PACVD–Plasma Assisted Chemical Vapor Deposition

PCE–Perchloroethylene

PDP–Plasma Display Panel

PECVD–Plasma Enhanced Chemical Vapor Deposition

PEEK–Polyethyletherketone

PEI–Polyetherimide

PEL–Permissible Exposure Limits

PET–Polyethylene Terephtalate (polyester)

PERC–Perchloroethylene

PFD–Process Flow Diagram

PFPE–Perfluorinatedpolyether

PIII–Plasma Immersion Ion Implantation

PLD–Pulsed Laser Deposition

PM–Preventive Maintenance

PMS–Pulsed Magnetron Sputtering

PO–Purchase Order

PP–Polypropylene

PSG–PhosphoSilicate Glass

PLD–Pulsed Laser Deposition

PVA–Polyvinyl Alcohol

PVC–PolyVinyl Chloride

PVD–Physical Vapor Deposition

PWB–Printed Wiring Board

p–parallel (Example: p wave)

pH–Pouvoir Hydrogene

ppm–Parts per million.

ppmbv–Parts per million by volume

Q–charge in coulombs

QA–Quality Assurance

QC–Quality Control

QCM–Quartz Crystal Monitor

R–Resistance

R_a–Roughness (average)

R_{max}–Roughness (maximum)

R_s–Sheet resistance, Spreading resistance

RAM–Random Access Memory

RED–Reflection Electron Diffraction

RBS–Rutherford Backscattering Spectrometry

RFI–Radiofrequency Interference

RHEED–Reflection High Energy Electron Diffraction

RIBE–Reactive Ion Beam Etching

RIE–Reactive Ion Etching

RFQ–Request for Quotes

RGA–Residual Gas Analyzer

RH–Relative Humidity

RIBE–Reactive Ion Beam Etching

RIE–Reactive Ion Etching

RMOS–Refractory Metal-Oxide Semiconductor

RO–Reverse Osmosis

ROM–Read-Only Memory

ROW–Rest of World

RPE–Reactive Plasma Etching

RT–Room Temperature

RTA–Rapid Thermal Annealing

RTCVD–Rapid Thermal CVD

RTN–Rapid Thermal Nitridation

RTP–Rapid Thermal Processing

rf–radio frequency

rms–root mean square

rpm–revolutions per minute

rps–revolutions per second

SACVD–Sub-Atmospheric CVD

SAD–Selected Area Diffraction

SAE–Society of Automotive Engineers

SAMPE–Society for the Advancement of Materials and Processing Engineering

SAW–Surface Acoustic Wave

SCM–Scanning Capacitance Microscope

SCSI–Small Computer Systems Interface

SEAM–Scanning Electron Acoustic Microscope

SEI–Secondary Electron Image

SEM–Scanning Electron Microscopy

SEMI–Semiconductor Equipment and Materials International

SI–Système International d'Unités

SIAM–Scanning Interferometric Aperatureless Microscope

SIMOX–Separation by Implanted Oxygen

SIMS–Secondary Ion Mass Spectrometry

SIP–Sputter Ion Plating

SIS–Semiconductor-Insulator-Semiconductor

SLAM–Scanning Laser Acoustic Microscope

SLAR–Single Layer Aintireflection

SMART–Self-Monitoring, Analysis and Reporting Technology

SME–Society of Manufacturing Engineers

SMIF–Standard Mechanical Interface

SMT–Surface Mount Technology

SOG–Spin-On-Glass

SPC–Statistical Process Control

SPE–Solid Phase Epitaxy

SPIE–International Society for Optical Engineering

SQUID–Superconducting Quantum Interference Device

SRAM–Static Random Access Memory

SRM–Standard Reference Material

SSMS–Spark Source Mass Spectrometry

STEL–Short Term Exposure Limits

STEM–Scanning Transmission Electron Microscopy

SThM–Scanning Thermal Microscopy

STI–Shallow Trench Isolation

STM–Scanning Tunneling Microscopy

STP–Standard Temperature (0ºC) and Pressure (760 Torr)

SVC–Society of Vacuum Coaters

SWP–Short Wavelength Pass filter

SZM–Structure-Zone-Model

s–second, perpendicular (as in s-wave)

sccm–standard cubic centimeters per minute

sccs–standard cubic centimeters per second

scf–standard cubic feet

scm–standard cubic meters

sg–specifc gravity

slm–standard liters per minute

TA–Thermal analysis

TA-MS–Thermal Analysis with Mass Spectrometry

TC–Thermocouple, Thermocompression

TCA–1,1,1-trichloroethane (or methyl chloroform)

TCE–Trichloroethylene ($CHCl{:}CCl_2$), Thermal Coefficient of Expansion

TCLP–Toxicity Characteristic Leaching Procedure

TCP–Transformer-Coupled Plasma

TCR–Temperature Coefficient of Resistivity

TD–Transverse Direction

TEM–Transmission Electron Microscopy

TFI–Thin-Film Inductive

TFT–Thin Film Transistor

TGA–Thermogravimetric Analysis

TGA-MS–ThermoGravametric Analysis with Mass Spectrometry

TIS–Total Integrated Scatter

TLV–Threshold Limit Values

TMDSO–Tetramethyldisiloxane

TWA–Time Weighted Average

TWM–Thermal Wave Microscopy

TZM–Alloy of titanium, zirconium and molybdenum

UBM–Unbalanced Magnetron

UCHF–Ultra-Clean High Flow

UF–Ultra-Filtration

UHP–Ultra-high Purity

UHV–Ultra-high Vacuum

ULPA–Ultra-low Permeation Air. See also *HEPA*

ULSI–Ultra-large Scale Integration

uPVC–Unplasticized Polyvinyl Chloride

UPW–Ultra-pure Water

USPTO–US Patent and Trademark Office

UTS–Ultimate Tensile Strength

UV–Ultraviolet

u–unified atomic mass unit

V–volt; Voltage (as in CV measurements)

VAR–Vacuum Arc Remelted

VCR–Voltage Coefficient of Resistance

VEPA–Very-high Efficiency Particulate Air (filter)

VHV–Very High Vacuum

VIM–Vacuum Induction Melted

VLR–Visible Light Reflection

VLT–Visible Light Transmission

VOC–Volatile Organic Compounds

VPE–Vapor Phase Epitaxy

VUV–Vacuum UltraViolet

v–velocity

W–watt

WDX–Wavelength Dispersive X-ray Analysis

WVTR–Water Vapor Transmission Rate

XES–X-ray Energy Spectroscopy

XPS–X-ray Photoelectron Spectroscopy

XRD–X-ray Diffraction

XRF–X-ray Fluorescence

XRM–X-ray Microanalysis

XRT–X-ray Topography

XUHV–Extra UltraHigh Vacuum

Y–Young's Modulus

Z–Atomic number of an element

ZAO–Aluminum-doped Zinc Oxide

ZD–Zero Defects

Miscellaneous

α–optical adsorption coefficient (cm^{-1}); amorphous

Ω–ohm

μ–micron

μm–micrometer

ν–frequency

λ–Wavelength

i–Prefix used to indicate that the film was formed using a beam-type film-ion deposition process. Example i-C, i-BN.

N–Normal

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