

# Properties of Silicon and Gallium Arsenide

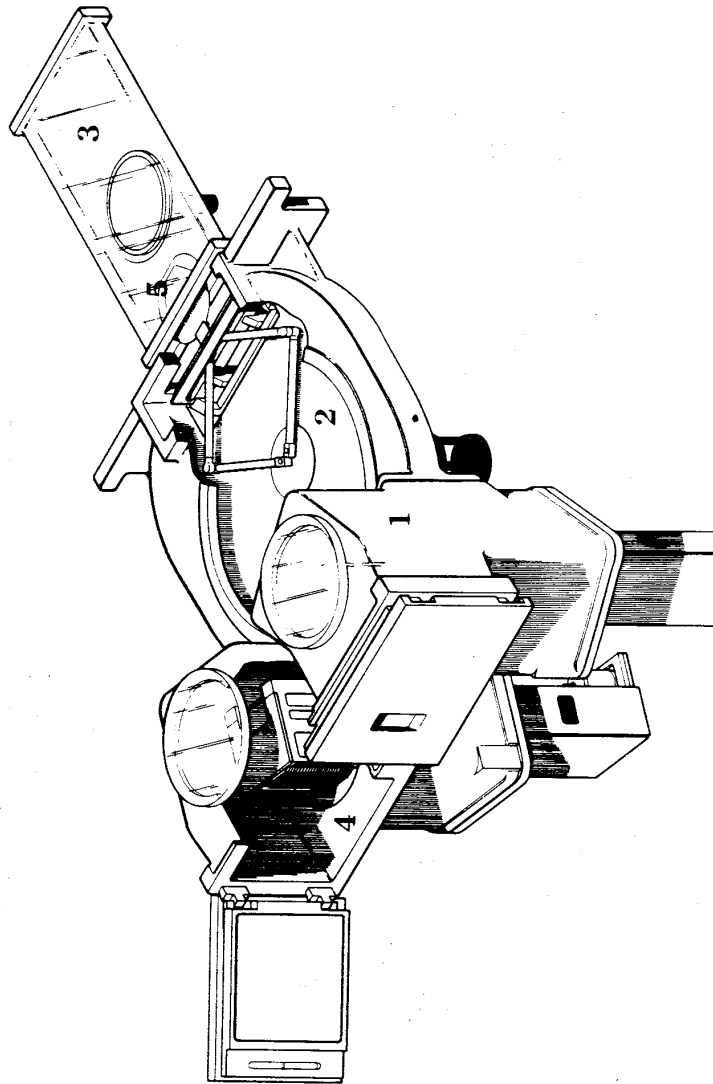
| Property                                                   | Silicon               | Gallium Arsenide      |
|------------------------------------------------------------|-----------------------|-----------------------|
| Crystal structure                                          | Diamond               | Zincblende            |
| Lattice constant (Å)                                       | 5.431                 | 5.646                 |
| Distance between neighboring atoms (Å)                     | 2.36                  | 2.44                  |
| Atoms or molecules/cm <sup>3</sup>                         | $5 \times 10^{22}$    | $2.21 \times 10^{22}$ |
| Density (g/cm <sup>3</sup> )                               | 2.328                 | 5.32                  |
| Melting point (°C)                                         | 1412                  | 1238                  |
| Thermal expansion coefficient (300 °K)                     | $2.6 \times 10^{-6}$  | $6.86 \times 10^{-6}$ |
| Thermal conductivity (W/cm-°C)                             | 1.5                   | 0.46                  |
| Energy gap (eV)                                            | 1.11                  | 1.435                 |
| Relative permittivity                                      | 11.9                  | 13.1                  |
| Breakdown field strength (V/μm)                            | ≈30                   | ≈40                   |
| Intrinsic carrier concentration, cm <sup>-3</sup> (300 °K) | $1.45 \times 10^{10}$ | $8 \times 10^6$       |
| Effective density of states                                |                       |                       |
| Valence band (cm <sup>-3</sup> )                           | $1.04 \times 10^{19}$ | $7 \times 10^{18}$    |
| Conduction band (cm <sup>-3</sup> )                        | $2.8 \times 10^{19}$  | $4.7 \times 10^{17}$  |

Thipwan Fongsewan

19/08/2004

UNSW

PV Engineering



Schematic of a fully automatic, cassette-loaded, epitaxial reactor. Key: 1,4: Cassette ports; 2: wafer transfer chamber; 3: process chamber; 5: wafer handling mechanism.  
Courtesy of ASM Epitaxy, Phoenix, Arizona.

# VLSI FABRICATION PRINCIPLES

## Silicon and Gallium Arsenide

Second Edition

**SORAB K. GHANDHI**

Rensselaer Polytechnic Institute  
Troy, New York



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To my wife, Cecille  
and  
my sons, Khushro, Rustom, and Behram  
for making it all worthwhile

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## CHAPTER 8

### DEPOSITED FILMS

A large number of different kinds of deposited films are used in microcircuit technology today; moreover, the functions they perform are continually increasing, as are their variety. In recent years, this list has greatly expanded because of the new requirements imposed by different VLSI schemes. Both insulating and conducting films are used. The division is not rigid here, since some films are deposited in one of these forms, and later converted to the other by processing. Even the term "deposited" is not a rigid one, since some films are deposited in elemental form and later converted to their final form by chemical reaction.

Deposited films are conveniently categorized by the primary functions they are required to perform. Some of these functions are electronic in nature, yet others are process-oriented. Thus, a number of different types of films are used to provide an insulating, protective cover on which interconnections can be made. Some of these can be patterned for use as diffusion or ion implantation masks, while others can be used to provide the doping function itself. Yet other films make possible the use of greatly simplified processing schemes such as self-aligned gate technologies for MOS microcircuits.

Many films and film combinations can be used to form ohmic contacts, as well as interconnections between devices in a microcircuit. Some of these can also be used to perform device functions as in Schottky diodes, and in Schottky-gate field effect transistors.

The films to be described in this chapter can be deposited by an equally wide variety of techniques; indeed, most films can be formed by more than one method. For each film, the emphasis will be on those techniques which are favored in semiconductor usage.

Physical deposition techniques of practical interest include vacuum evapo-

ration, as well as d.c. and r.f. sputtering. The recent development of magnetron sputtering represents improvements over conventional sputtering methods, and provides increased growth rates. In addition, reactive sputtering is also used in some applications where the desired film is not elemental in nature, but is a compound. All of these sputtering techniques share the advantage that substrates can be cleaned (by back-sputtering) prior to film deposition. Ion beam deposition is yet another technique and has the following advantages: (a) relative freedom from contamination and (b) independent adjustment of system parameters such as substrate temperature, beam energy, and current density. Equipments for physical deposition of films form a highly specialized branch of manufacturing technology and have been considered in detail elsewhere [1].

The primary emphasis on chemical techniques has been on chemical vapor deposition (CVD) processes, which were considered in detail in Chapter 5. Many of the systems and techniques developed for vapor phase epitaxy can be directly used (or modified for use) to deposit a wide variety of insulating and conducting films. These systems are often operated at low pressure ( $\leq 0.1$  torr); this results in increasing the diffusivity of the reactant species, and leads to greater uniformity and throughput than does operation at atmospheric pressure. Consequently, recent emphasis on production techniques is in this area. Finally, the use of plasma enhancement allows reactions to be carried out by energetic species with an electron temperature of around 10,000 K. As a result, growth can be accomplished at greatly reduced temperatures by these techniques.

In this chapter, the salient features of various deposition techniques will be described in order to highlight their advantages and disadvantages. Next, we shall consider the characteristics of importance in the selection of these deposition methods. Finally, we shall consider the many films which are used in microcircuit fabrication, in terms of the functions which they provide in an integrated circuit.

Tables of relevance to this topic are assembled at the end of this chapter for ready reference.

## 8.1 FILM DEPOSITION METHODS

The principal techniques for depositing films are vacuum evaporation, sputtering, and chemical vapor deposition. Wet chemical plating is also used in some applications. Each of these techniques is a highly specialized field in itself, and has been the subject of much research and development. Here, we shall confine ourselves to their basic operating principles, in order to assess their applicability in microcircuit fabrication.

### 8.1.1 Vacuum Evaporation

Perhaps the simplest technique for depositing a material in thin film form is by vacuum evaporation. In this process, the material to be evaporated is heated in

an evacuated chamber so that it attains a gaseous state. Vapors of this material traverse the space from the source to the substrate, on which they eventually land. In principle, therefore, it is identical to molecular beam epitaxy (MBE). The key differences, however, are that vacuum evaporators operate at higher base pressures, and handle multiple slices and with much higher deposition rates than their MBE counterparts. These differences will determine the suitability of these systems for any given application.

Metal deposition rates of  $0.5 \mu\text{m}/\text{min}$  are typically desired in vacuum evaporation. This necessitates that the equilibrium pressure of the evaporant [see Eq. (5.22)] be in the 10-mtorr range, and restricts the use to materials which can be evaporated from heated crucibles. Materials such as aluminum and gold are nearly ideal for this technique. On the other hand, materials such as tungsten and titanium have extremely low vapor pressures, and cannot be delivered in this manner. Extensive data on the vapor pressure versus temperature characteristics of a number of materials are available in the literature [2]. Figure 8.1 shows vapor pressure data for some materials of interest for microcircuit fabrication.

Electron-beam (e-beam) evaporation, whereby an intense beam of energy is applied locally to a target, can be used to develop a sufficiently large flux of evaporant from refractory materials. Here, the source is held in a water-cooled hearth, and evaporation occurs at a highly localized point on this source, while its bulk remains solid. Thus, there is no contamination from the crucible, as long as the e-beam is well designed, and only strikes the target during this process.

The use of an electron gun results in a point source, so that the flux pattern is Lambertian in nature, resulting in a nonuniform film thickness across the substrate. In multiple-slice systems, this nonuniformity can be minimized by rotating the slices during evaporation, and sophisticated planetary motion systems are used for this purpose. In addition, the point of impact of the e-beam is moved around electronically during the evaporation, so as to simulate a large area source.

Electron-beam sources can be used with refractory as well as nonrefractory materials. Often, multiple hearths are incorporated into these systems, to permit the deposition of multilayer films in a sequential manner, without the need to break vacuum and with very little system contamination.

The path taken by the evaporant to the substrate should be one that is collision-free, to prevent agglomeration of material in the gas phase. Thus, its length should be less than the mean free path. From Eq. (5.19b), it can be shown that this mean free path is about  $10^3$  cm, for a system pressure of  $10^{-5}$  torr. However, the typical vacuum evaporator must be capable of being pumped down to  $10^{-7}$  torr, to minimize the residual contamination level in the system. Many pumping techniques can be used for this purpose. Their technology [3] is an art in itself and is beyond the scope of this book.

Vacuum conditions imposed by the mean free path requirement place additional restraints on the choice of materials which can be deposited by this method. For example, the vapor pressure of materials such as cadmium and zinc are so high that they evaporate too rapidly, and tend to contaminate the entire system during this process.

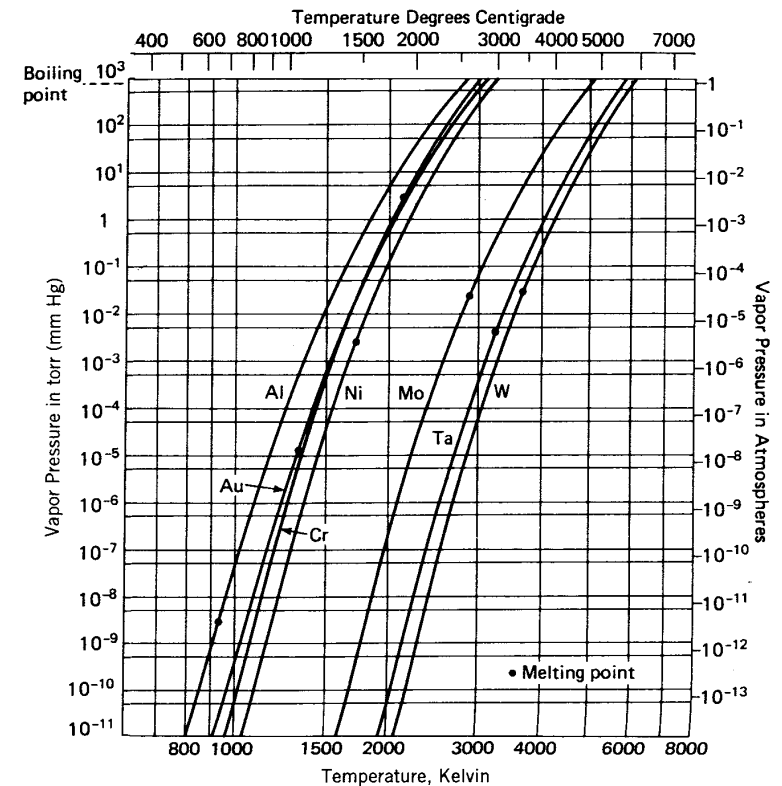


Fig. 8.1 Vapor pressure curves for selected materials. Adapted from [2].

During vacuum evaporation, substrates are essentially unheated, except for radiation from the evaporant source. In some systems, internal infrared heaters are used when it is desired to conduct the evaporation at elevated temperature.

The energy associated with thermal evaporation is in the 0.1- to 0.15-eV range. Thus, this process results in no damage to the substrate surface. This is a significant advantage in the deposition of films over gate oxides. However, this advantage is not present with e-beam evaporation, where relatively high voltages ( $\geq 10$  kV) are used for beam formation and direction. This produces x-rays, which cause damage in the substrate on which the film is deposited. With gate oxides, there is a significant increase in the fixed oxide charge as well as in the density of interface traps when e-beam evaporation is used.

Vacuum evaporation of alloys with accurately controlled composition is extremely difficult because of the vapor pressure dissimilarity of their separate components. In general, therefore, the composition of the alloy film will

be quite different from that of the source, and this difference will vary with time as the source gets preferentially depleted. Multiple crucible sources, one for each element, have been used but these require extremely precise temperature control for satisfactory operation. Although used in MBE systems, they are not practical in commercial evaporators. The control of evaporant flux from an electron gun is sufficiently poor so that the alloy composition control is not satisfactory by this means, either.

Finally, *in situ* thermal substrate cleaning, although used in MBE, is not practical in vacuum evaporators because of their multiple-slice capability. Thus, adhesion of the film to the substrate is sometimes imperfect. This is not a problem with aluminum films on  $\text{SiO}_2$ , since bonding is accomplished by local reaction of these materials. With noble metals such as gold, however, it is customary to first evaporate a thin layer of a reactive material, which serves as a "glue" between the evaporant and the substrate. Chromium and titanium are often used for this purpose.

### 8.1.2 Sputter Deposition

Sputter deposition, or *sputtering*, is considerably more versatile than vacuum evaporation, and is extensively used in the deposition of thin films in micro-circuit technology. The reasons for its popularity are (a) the ability to deposit a wide variety of metals and insulators, as well as their mixtures, (b) the replication of target composition in the deposited film, and (c) the capability for *in situ* cleaning of the substrate prior to film deposition.

Sputter deposition is carried out in a self-sustained glow discharge which is created by the breakdown of a heavy inert gas such as argon. The physics of this process is illustrated in Fig. 8.2a. Here, a d.c. electric field is impressed across two water-cooled electrodes which are located in this gas. At sufficiently low electric field intensities, a very small current will flow, primarily by the transport of electrons between these electrodes. These electrons may be produced by photoemission or by cosmic ray stimuli, and are always present to some degree in any gaseous medium.

Transport of electrons between the electrodes will result in some collisions with the gas molecules, so that ionization will occur in those encounters where a sufficiently large amount of energy is transferred to the gas. The products of these few ionizing collisions (namely,  $\text{Ar}^+$  and electrons) are themselves accelerated (in opposite directions) because of the electric field, so that they can also enter into collisions with neutral argon molecules, thus resulting in an avalanche multiplication effect. The actual magnitude of this effect\* will depend on the electric field intensity since this determines the acceleration of the electrons and  $\text{Ar}^+$ , and on the gas pressure which establishes the mean free path for collisions. It will depend also upon the distance between electrodes,

\*About  $5 \text{ argon ions cm}^{-1}$  for an electron energy of 1 keV, at a pressure of 1 torr.

since the number of collisions per unit length traveled is reciprocally related to the mean free path.

Figure 8.2a shows this situation, where multiple electrons reach the anode and the  $\text{Ar}^+$  ions reach the cathode. At sufficiently high applied voltages, some of these  $\text{Ar}^+$  ions can eject secondary electrons from the cathode, thus adding to the supply of electrons which contribute to the avalanche multiplication process. This can eventually lead to gaseous breakdown [4] with the current being limited by the circuit impedance. For this condition,  $\text{Ar}^+$  ions bombard the cathode, resulting in sputtering\* of its surface material by momentum transfer. In addition, secondary electrons\*\* emitted at the cathode participate in sustaining the discharge by ionizing collisions with argon molecules.

Figure 8.2b shows the nature of the discharge. The most important region here is the Crooke's dark space across which nearly all of the applied voltage is dropped. Both ions and electrons created at breakdown are primarily accelerated across this region. Its thickness  $d$  is related to the chamber pressure  $p$ ; for argon the  $pd$  product is about 0.4 torr-cm.

\*This sputtering process is of technological importance for the etching of materials, and will be taken up in detail in Chapter 9.

\*\*About one electron per ten incident argon ions.

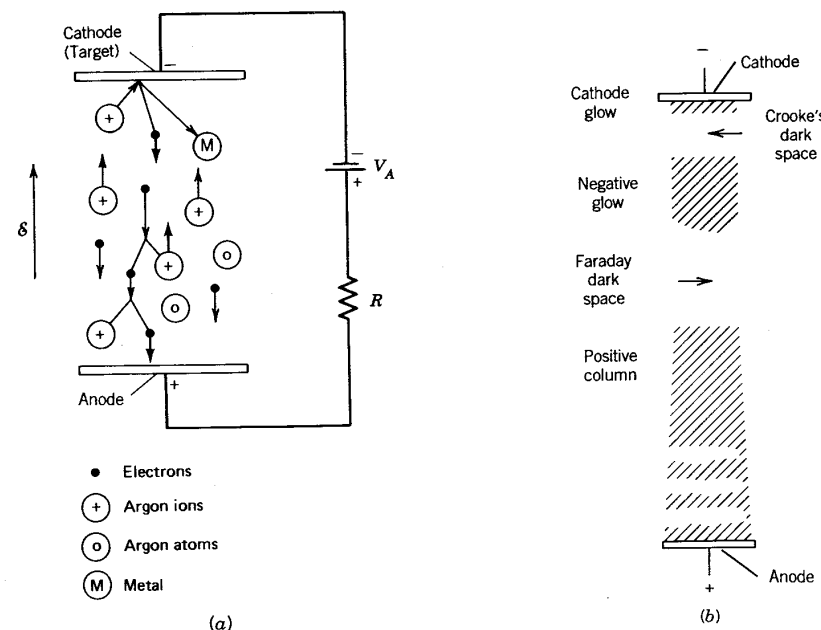


Fig. 8.2 Sputtering in a d.c.-excited glow discharge.

The positive column and the Faraday dark space are not necessary for the operation of the discharge; for all practical purposes, they serve merely as electrical connections between the anode and the negative glow region. Consequently, it is possible to shorten the anode-cathode spacing by moving the anode into this negative glow region. This results in a higher breakdown voltage, since it eliminates part of the region where collisions can take place. The principles outlined here for the d.c. glow discharge can also be extended to discharges with r.f. excitation.

It should be emphasized that nearly all of the voltage drop is in the vicinity of the cathode, resulting in its bombardment by high-velocity  $\text{Ar}^+$  ions. On the other hand, the anode, on which deposition of the material which constitutes the cathode (target) occurs, is in a relatively field-free region. Atoms ejected from the cathode are mostly neutral, although both positive- and negative-charged species are also produced. They have an energy spread of 0–20 eV, and diffuse to the anode or the chamber walls, where they arrive in a relatively nondirected manner. Sputter deposition of the material which constitutes the cathode (target) occurs on substrates placed on the anode; good adhesion is achieved because of ion mixing, resulting from this energy spread.

With d.c. sputter deposition, it is necessary that positive ions impinging on the target surface have an opportunity to recombine with electrons to prevent charge accumulation on the surface. While discharging arrangements can be provided to minimize this problem, it can be avoided if the discharge is maintained by an r.f. field. This approach is most commonly used, since it is equally effective with both conducting and insulating substrates.

Radio frequency sputtering is usually carried out with a 1- to 3-kV peak-to-peak r.f. potential. Excitation is commonly provided at 13.56 MHz, which is internationally assigned for equipment usage. A schematic arrangement of this type of system is shown in Fig. 8.3. Here, advantage is taken of the diode-like character of the discharge to produce a self-bias, so that the electrodes take on the role of anode and cathode (target) as shown. Sputter deposition is carried out by placing substrates on the anode, as before.

A wide variety of conducting and insulating materials, as well as their mix-

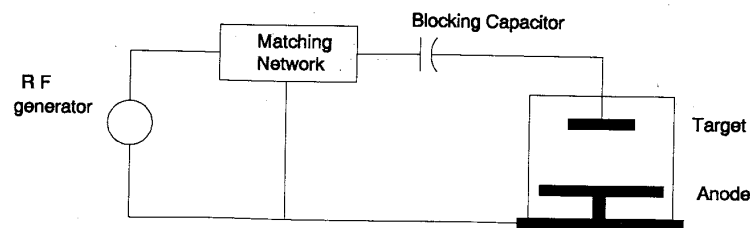


Fig. 8.3 Schematic of an r.f. sputtering system.

tures, can be deposited by sputtering. In most cases, targets for this purpose are generally made of mixtures of the components to be deposited, which are hot-pressed into the form of a disc. This disc is bonded to a copper cathode which is water-cooled; elaborate shielding is provided to prevent sputter deposition of copper from this cathode.

Upon system evacuation, a large amount of out-gassing occurs from the target because of its porous character. Further out-gassing occurs upon bombardment during operation. This results in considerable variability from run to run, unless the sputtering system is maintained under vacuum at all times, and substrates introduced via a load-lock arrangement.

A key advantage of sputtering over vacuum evaporation is that the alloy content of a multicomponent target is replicated in the source film, even if it consists of materials with widely different sputter yield. By way of example, consider a two-component target,  $A-B$ , in which the sputtering yield of  $A$  is much larger than that of  $B$ . On initial use, the film will have an excessively large concentration of  $A$ , and the surface layers of this target will become preferentially depleted of this material. Consequently, the concentration of  $A$  in the film will fall as sputter deposition proceeds. This process will continue until steady state is reached, at which point the composition of the film and the bulk of the target will become identical. Typically, the thickness of the altered layer is a few tens of angstroms for metal alloys, and can be as thick as 1000 Å for targets of oxide mixtures [5]. Thus, the steady-state condition for the target is reached shortly after it is put into operation for the first time [6].

In a d.c. sputtering system, it is possible to reverse system polarity, and thereby etch the substrate prior to film deposition. This process, known as *back-sputtering*, is extremely useful for removing thin surface layers such as residual oxides, which can affect the electrical and mechanical properties of the film-substrate combination, or prevent adhesion of the film to the substrate.

Sputtering systems are normally operated at pressures around  $10^{-2}$  torr, which are considerably higher than those encountered during vacuum evaporation. Thus, they are relatively "dirty" in comparison, unless considerable care is taken to provide a clean pumping arrangement. Often, this includes the incorporation of cryogenic traps and the use of turbomolecular pumps, which are oil-free. In addition, high gas flows are commonly used to continually sweep impurities out of the sputtering chamber. Base pressures of these systems are comparable to those used with vacuum evaporation—that is, in the  $10^{-7}$  torr range.

The biggest disadvantage of sputtering is that it results in damage to the substrate, which is not completely free from impact by high-energy species. Sputtering is thus to be avoided in situations such as the deposition of materials on a gate oxide. In some cases, heating of the substrate (in addition to that which is intrinsic to the sputter deposition process) is used to anneal this damage as it is created. This is usually provided by resistive or infrared elements.

### 8.1.2.1 Magnetron Sources

In sputtering systems of the type described here, only a small fraction of electrons emitted from the target collide with argon ions, whereas the rest are collected at the anode, where they cause unwanted heating. The use of a magnetic field, to confine these electrons near the target surface, greatly increases the possibility of ionizing collisions with the argon gas molecules. This, in turn, increases the  $\text{Ar}^+$  concentration, and hence the film deposition rate. This process is known as *magnetron sputtering*.

Detailed descriptions of a wide variety of both cylindrical and planar magnetron sputtering targets are provided in the literature [1]. Their principle is illustrated in Fig. 8.4 for two particular configurations. With both circular and rectangular sources, a magnetic field strength of 100–200 gauss is used, resulting in field lines which confine electrons to the region embraced by them. The discharge region is thus in the shape of a toroid or an elongated ring, with extensive sputtering of the target in these regions. Substrates are usually placed on a rotating anode in order to obtain uniform film deposition.

### 8.1.3 Chemical Vapor Deposition

This topic has been covered in Chapter 5 in the context of epitaxial growth. As with vapor-phase epitaxy (VPE), chemical vapor deposition (CVD) involves transport of reactant species into the reactor, reaction at the substrate, and removal of reaction products. The process can be carried out in hot or cold wall reactors, at atmospheric pressure (APCVD) as well as at low pressure (LPCVD).

APCVD is usually conducted in cold wall reactors, since many of the reactions involved in the deposition of thin films are pyrolytic in character. Resistive heating of the susceptor is often used, since growth temperatures are usually

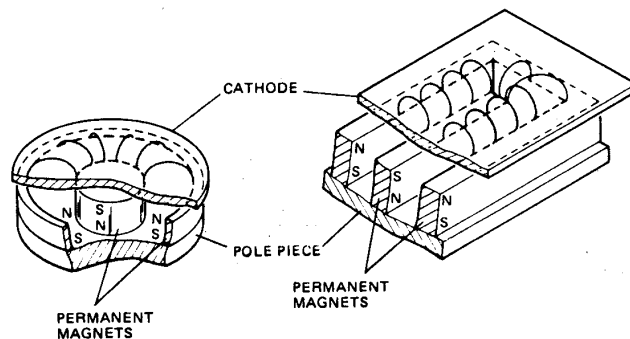


Fig. 8.4 Circular and rectangular magnetron sputtering targets. The curved lines represent magnetic field lines. From Vossen and Kern [1]. Reprinted with permission from Academic Press.

lower than those encountered with VPE. Systems of the type shown in Fig. 5.13a are used for this application. Continuous deposition systems, using muffle furnaces, are also available for high-volume applications.

In VPE, the emphasis is on the growth of single-crystal films with a high degree of crystal quality. For applications considered in this chapter, however, uniformity and high throughput are the overriding factors. Films are generally polycrystalline or amorphous so that high growth rates can be used; although a clean reactor environment is always desirable, the levels of purity and freedom from contamination which are essential for VPE are seldom required (or met) in CVD systems. LPCVD is a very attractive approach for the growth of these films.

Following along the lines of Chapter 5, the growth rate of a film is given by

$$\frac{dx}{dt} = \frac{N_g}{n} \left( \frac{hk}{h+k} \right) \quad (5.30)$$

where  $N_g$  is the reactant concentration in the gas phase,  $n$  is the number of atoms (or molecules) of the grown material in unit volume,  $k$  is the reaction rate constant, and  $h$  is the mass transfer coefficient which is directly proportional to the diffusivity,  $D$ . Here,

$$k = k_0 e^{-E_a/RT} \quad (8.1a)$$

$$h = \frac{D}{\delta_D} \quad (8.1b)$$

where  $E_a$  is the activation energy of the reaction at the substrate, and  $\delta_D$  is the thickness of the diffusive boundary layer.

The diffusivity, and hence  $h$ , varies inversely with system pressure. Operation at 0.5 torr, for example, results in an increase in  $h$  by a factor of 1520 from its value at atmospheric pressure. Now,

$$\frac{dx}{dt} \approx \frac{N_g k}{n} \quad (8.2a)$$

$$\approx \frac{N_g k_0}{n} e^{-E_a/RT} \quad (8.2b)$$

since  $h \gg k$ .

There are two important consequences of this result. First, the growth rate across the slice is only a function of the temperature, and is thus independent of flow conditions in the reactor. Thus, films can be deposited on a very large number of slices, with a high degree of uniformity, provided that tight control is placed on temperature. This favors growth in a hot wall reactor, with multiple temperature-controlled zones. Slices can be closely spaced, to obtain a high

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## CHAPTER 9

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### ETCHING AND CLEANING

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Etching and cleaning processes are involved at many points in the microcircuit fabrication process. Thus, saw-cut slices of suitably oriented semiconductor material are first mechanically lapped to remove gross damage, and then chemically etched and polished to obtain an optically flat, damage-free surface. Often, this involves the removal of many microns of surface material. Next, slices are chemically cleaned and scrubbed to remove contaminants produced by handling and storing, before being covered with an initial protective layer of thermally grown SiO<sub>2</sub> (for silicon-based microcircuits) or deposited Si<sub>3</sub>N<sub>4</sub> (for GaAs circuits). Etching processes, in conjunction with patterning, are used to cut openings in this protective film through which implants or diffusion are made to form the semiconductor regions. This process is repeated until all the components are formed.

Further etching and patterning processes are used to delineate one or more layers of metallization. This is often followed by protective coatings of deposited phosphosilicate glass (PSG) or Si<sub>3</sub>N<sub>4</sub>. Again, both etching and patterning processes are used to cut holes for access to the bonding pads, to which leads can be attached.

The term *etching* is used to describe all techniques by which material can be uniformly removed from a wafer as in surface polishing, or locally removed as in the delineation of a pattern for a microcircuit. It also includes chemical machining of a semiconductor as part of the fabrication process, as well as the delineation of surface features such as defects.

In addition to semiconductors, wet chemical etching is used for the dissolution of a wide variety of grown and deposited films of the type described in Chapters 7 and 8. This process involves simple dissolution of the material, as

well as its conversion to a soluble species which can be dissolved in the etching medium.

Dry processes are also used for material removal, and can be physical or chemical in character. Physical etching processes involve the removal of material by momentum transfer from a rapidly moving inert projectile (usually argon). *Ion milling* is an important mechanical etching process of this type, and has been [1] appropriately referred to as 'sandblasting on an atomic scale.' Another process that is often used is *sputtering*, which is similar in its essential features to ion milling. Both of these techniques require the formation of a gas discharge to produce high-velocity argon ions. However, chemically reactive energetic species are not involved in these processes, which are essentially physical in nature.

Dry chemical etching processes are sometimes carried out in the gas phase, and are restricted to special situations, such as the *in situ* etching of silicon prior to epitaxy, as described in Chapter 5. They can be made considerably more versatile if they can be carried out at low temperature, by means of energetic species of the gaseous reactants. These species can be produced by passing the reactant through a gas discharge, and delivering it downstream to the material to be etched.

Finally, the advantages of both dry physical and chemical processes can be combined by immersing the material to be etched directly in the gas discharge, so that it is subjected to both reactive chemical species and ion bombardment. The dominant effect of ion bombardment is to weaken the chemical bonding of the surface material, so that it can be chemically attacked by the energetic species. Here, the atom-substrate reactions of the energetic species are enhanced by the ion bombardment, so that the etch rate is usually greater than the sum of the two separate processes. This process is known as *reactive ion etching*.

This chapter will describe the many etching processes that are used in the fabrication of microcircuits. Both wet and dry processes will be considered, the latter being especially important for VLSI fabrication technology. Pattern transfer processes, which are often used in conjunction with etching, will be described in the following chapter.

The cleaning of semiconductor surfaces will also be treated here. This is necessary to remove a variety of organic and inorganic contaminants, often of unknown origin, which are present on the as-purchased semiconductor surface. These include (a) films of native oxide, airborne contaminants such as common salt and bacteria and (b) chemical residues such as oil and plasticizer films from the packages in which wafers are shipped. Cleaning between processing steps is also important in order to avoid the introduction of contaminants.

Many of these cleaning processes are closely related to etching, in that they involve some removal of the semiconductor surface; however, this is not their primary intent. They play an important role in microcircuit fabrication technology.

## 9.1 WET CHEMICAL ETCHING

Wet chemical etching of any material can be considered as a sequence of three steps: transport of the reactant to the surface, reaction at the surface, and movement of reaction products into the volume of the etchant solution. Each of these can serve as the rate limiter and thus dominate the overall process.

An etch process which is limited by the rate of surface reaction will tend to enhance surface roughness and promote faceting, since the surface activity is a strong function of localized defects and crystallographic orientation. On the other hand, etching can be limited by the rate of diffusion of the etchant through a stagnant layer which covers the surface. This results in an etch which is polishing in character; now, a rough surface with many protuberances and facets will tend to become smooth in this process.

Removal of the reaction products can also be a rate-limiting factor. In practice, this determines the "equilibrium" amount of reaction product that is left on the substrate. It also serves as an additional layer to the stagnant film through which reactant must diffuse before etching occurs; thus, it can slow down the etch rate.

In all cases, the etch rate can be altered by rapid stirring to aid in removal of reaction products and gas bubbles, or by increasing the temperature of the etch solution. Typically, a doubling of etch rate occurs with each 10°C rise in temperature. As a result, the development of etch processes for use in a manufacturing environment requires that attention be paid to these factors, in addition to the choice of chemicals and their concentrations.

The temperature-dependent characteristics of etching can be used to advantage in situations where it is essential to keep residual surface contamination to a minimum. Here, the strategy is to use a high dilution with deionized water, and maintain a reasonable etch rate by operating at an elevated temperature. In other situations, where precise etch control is desired, the use of a cooled etch solution is indicated.

A number of chemical reagents, and their mixtures, are used for etching purposes. Many of these are available in "transistor-grade" purity and are preferred in order to minimize contamination of the semiconductor during processing. Water is an intrinsic component of all of these reagents. Moreover, deionized water is invariably used as a diluent. The compositions of commonly used aqueous reagents are given in Table 9.1. This table, as well as others on this topic, are collected at the end of this chapter for ready reference.

### 9.1.1 Crystalline Materials

Single-crystal silicon and GaAs fall into this category; both exhibit long-range order, and their etching can be either isotropic or anisotropic in character. Etching by wet chemicals usually proceeds by their oxidation, followed by the chemical dissolution of the oxide (or oxides). Both of these processes are carried out simultaneously by a mixture of the reagents in the same etching solu-