

Chemical Vapor Deposition

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7.1 Introduction

Chemical vapor deposition (CVD) is parent to a family of processes whereby a solid material is deposited from a vapor by a chemical reaction occurring on or in the vicinity of a normally heated substrate surface. The resulting solid material is in the form of a thin film, powder, or single crystal. By varying experimental conditions, including substrate material, substrate temperature, and composition of the reaction gas mixture, total pressure gas flows, etc., materials with a wide range of physical, tribological, and chemical properties can be grown. A characteristic feature of the CVD technique is its excellent throwing power, enabling the production of coatings of uniform thickness and properties with a low porosity even on

Table 7.1: Summary of chemical vapor deposition (CVD) process family

Type	Pressure range	Description
Atmospheric pressure CVD (APCVD)	High-atmospheric	Processes at atmospheric pressure
Low-pressure CVD (LPCVD)	Low	Processes at subatmospheric pressures
Ultrahigh vacuum CVD (UHVCVD)	Typically below 10^{-6} Pa ($\sim 10^{-8}$ torr)	Processes at a very low pressure
Aerosol-assisted CVD (AACVD)		Precursors are transported to the substrate by means of a liquid/gas aerosol, which can be generated ultrasonically
Direct liquid injection CVD (DLICVD)		Precursors are in liquid form (liquid or solid dissolved in a convenient solvent). Liquid solutions are injected in a vaporization chamber towards injectors (typically car injectors). Then the precursor's vapors are transported to the substrate as in classical CVD process
Microwave plasma-assisted CVD (MPCVD)		
Remote plasma-enhanced CVD (RPECVD)		Utilizes a plasma to enhance chemical reaction rates of the precursors, and allows deposition at lower temperatures
Atomic layer CVD (ALCVD) or ALD		Deposits successive layers of different substances to produce layered, crystalline films
Hot wire CVD (HWCVD)		Also known as catalytic CVD (Cat-CVD) or hot filament CVD (HFCVD). Uses a hot filament to chemically decompose the source gases
Metal-organic chemical vapor deposition (MOCVD)		Based on metal-organic precursors
Hybrid physical-chemical vapor deposition (HPCVD)		Vapor deposition processes that involve both chemical decomposition of precursor gas and vaporization of a solid source
Rapid thermal CVD (RTCVD)		Uses heating lamps or other methods to rapidly heat the wafer substrate
Vapor-phase epitaxy (VPE)		

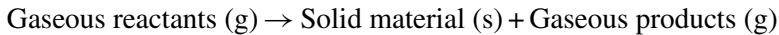
substrates of complicated shape. Another important feature is the capability of localized, or *selective* deposition, on patterned substrates.

CVD and related processes are employed in many thin film applications, including dielectrics, conductors, passivation layers, oxidation barriers, conductive oxides, tribological and corrosion-resistant coatings, heat-resistant coatings, and epitaxial layers for microelectronics. Other CVD applications are the preparation of high-temperature materials (tungsten, ceramics, etc.) and the production of solar cells, high-temperature fiber composites and particles of well-defined sizes. Recently, high T_c superconductors, and more recently carbon nanotubes, have also been made by this technique [1]. Since oxygen activity in the vapor can be precisely controlled during the deposition, no annealing in oxygen is needed to achieve superconductivity.

There exists a multitude of CVD processes, listed in Table 7.1. In thermally activated CVD (TACVD), the deposition is initiated and maintained by heat. However, photons, electrons, and ions, as well as a combination of these (plasma activated CVD), may induce and maintain CVD reactions. In this chapter, the underlying principles of TACVD are introduced. In addition, large-area deposition and selective CVD on patterned substrates are discussed.

7.2 Important Reaction Zones in CVD

In every CVD process, gaseous reactants are admitted into a reactor (Figure 7.1). Near or on a heated substrate surface the following chemical reaction occurs:



Five important reaction zones related to gas flows and temperature are developed during the CVD process, as shown in Figure 7.2. The properties of CVD materials are affected by the interacting processes occurring in these reaction zones. In a CVD process, a main gas flow (the reaction gas mixture) passes over the substrate/coating surface. Fluid dynamics of the process results in a more or less stagnant boundary layer occurring in the vapor adjacent to the

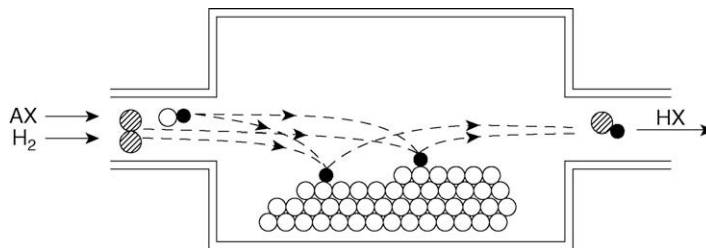


Figure 7.1: The principle of CVD.

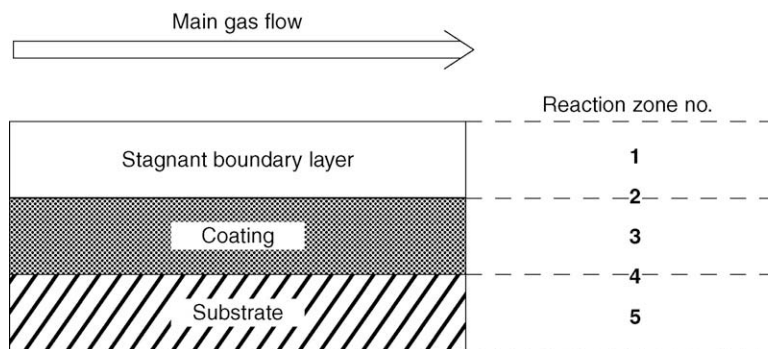


Figure 7.2: Important reaction zones in CVD.

substrate/coating. During the deposition process, the gaseous reactants and the gaseous reaction products are transported across this boundary layer. In reaction zone 1 (Figure 7.2) as well as in the main gas stream, homogeneous reactions may occur in the vapor, which may lead to an undesirable homogeneous nucleation characterized by a flaky and non-adherent coating. In some cases, however, these reactions, when not accompanied by homogeneous nucleation, are favorable to the CVD process (e.g. CVD of Al_2O_3 [2], of B_{13}C_2 [3], and of Si [4]). Heterogeneous reactions occur in the phase boundary vapor/coating (zone 2). These reactions typically determine the deposition rate and properties of the coating. Relatively high temperatures can be used during CVD, leading to various solid state reactions (e.g. phase transformations, precipitation, recrystallization, grain growth) that can occur in zones 3–5. In zone 4, which is a diffusion zone, it is possible to form various intermediate phases. The reactions in this zone are important for the adhesion of the coating to the substrate.

7.3 Design of CVD Experiments

Because not all reactors are exactly alike, every CVD experiment is unique. However, some general aspects in the design of CVD experiments can be given. Design is usually an iterative procedure. For instance, the choice of the reaction gas mixture affects the design of the CVD system, the cleaning procedure, the adhesion of the coating, etc.

7.3.1 Classification of CVD Reactions

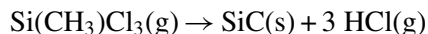
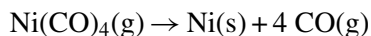
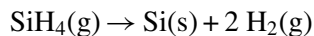
CVD processes frequently proceed by complex chemical reaction schemes. However, a general classification of use of CVD reactions can be made.

Thermal decomposition reactions or pyrolytic reactions are characterized by thermal dissociation of a gaseous compound AX into A (solid material) and X (gaseous

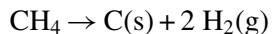
reaction product):



Thermal decomposition reactions normally result in relatively pure coatings. Examples of thermal decomposition reactions are given below:

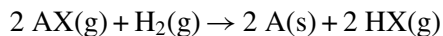


Processes like carburizing and nitriding are also classified in this reaction category. In carburizing, for instance, a carbon-carrying vapor species, e.g. methane, is allowed to react at/on a heated surface. Methane then decomposes in principle according to

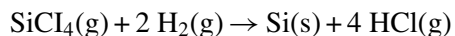
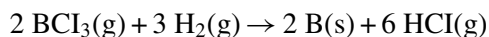
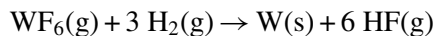


Deposited carbon reacts immediately with the substrate, yielding a solid solution of carbon in the substrate and/or, if they exist, carbides of the substrate material.

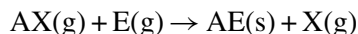
Reduction reactions, where hydrogen acts a reducing agent, are frequently used (see also *Coupled reactions* below):



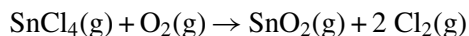
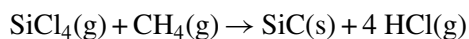
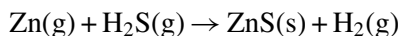
Straightforward reduction reactions are almost used exclusively in the CVD of elements.



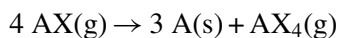
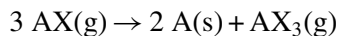
Exchange reactions are characterized by an element E replacing another element, for instance X, in the molecule AX according to



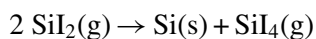
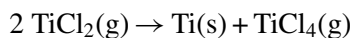
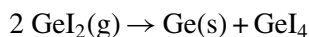
Examples of exchange reactions are:



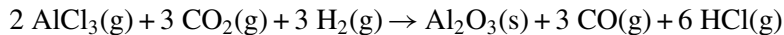
Disproportionation reactions are rarely used in CVD, and occur when the oxidation number of an element both increases and decreases through the formation of two new species. CVD of A from AX can be obtained in disproportionations such as



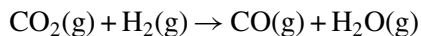
Examples of disproportionation reactions are



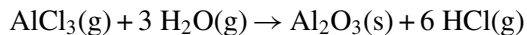
Coupled reactions are often used in CVD. The coupled CVD reaction of Al_2O_3 from AlCl_3 , CO_2 and H_2 can be described in an overall reaction:



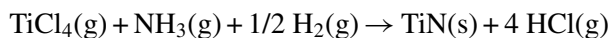
where the reaction in which water is formed



is coupled to the hydrolysis reaction



i.e. a reduction reaction is coupled to an exchange reaction [2]. Other examples of overall coupled CVD reactions are



In general, several options for preparing a thin film material by CVD exist. For practical reasons however, relatively few alternatives will remain after a critical evaluation of the requirements of the process (temperature, total pressure, compatibility with the substrate and the reactor, the reaction's gas mixture, costs, toxicity of the substances, etc.).

7.3.2 Thermodynamics

Thermodynamic calculations are a useful tool when selecting experimental conditions (temperature, total pressure, reaction gas composition) for deposition of a certain material, and also serve as a guide when changing the experimental conditions in a CVD process. A number of computer programs are in use for these calculations and there are now practically no limitations on the number of materials that can be included in the calculations. For reviews of computational methods, the reader is referred to [5–8].

Computer programs are typically based on the so-called *free energy minimization* technique. The free energy G is given by the following equation:

$$G = \sum_i n_i \mu_i$$

where n_i is the number of moles of a substance i and μ_i is the chemical potential. The chemical potential is defined as

$$\mu_i = \mu_i^0 + RT \ln a_i$$

where μ_i^0 is the reference chemical potential, and a_i is the activity. Assuming ideal gas conditions, the activity of the gaseous species may be expressed as its partial pressure

$$a_i = p_i = (n_i/n)P$$

where n is the number of moles in the gas phase, and P the total pressure. For pure condensed substances, activities are equal to unity.

Eriksson [9] developed a computer program (SOLGAS) based on the minimization of the free energy. This program became a prototype for many other equilibrium calculation programs. From the basic equations given above, the dimensionless quantity G/RT was defined (see equation below) and used in the calculations.

$$\frac{G}{RT} = \sum_{i=1}^m n_i^g \left[\frac{\mu_i^0}{RT} \right]_i^g + \ln P + \ln \frac{n_i^g}{n} + \sum_{i=1}^n n_i^s \left[\frac{\mu_i^0}{RT} \right]_i^s$$

Superscripts *g* and *s* refer to the gas phase and the solid phase, respectively. The value of μ_o/RT for a specific substance is calculated from

$$\frac{\mu_o}{RT} = \frac{(G^o - H_{298}^o)}{RT} + \frac{\Delta H_{f,298}^o}{RT}$$

where $(G_o - H_o)/RT$ = free energy function, and $H_{f,298}^o$ = heat of formation at 298.1 K.

By minimizing G/RT (or G) and using mass balance equations as subsidiary conditions, the equilibrium composition of a system can be calculated.

Input data for the calculations are the number of moles of the different reactants, total pressure, substrate temperature, different substances, and their thermochemical data. From the calculations, various quantities like the partial pressures of the vapor species, amounts of the different substances available for CVD, i.e. the yield, and thermodynamic functions (supersaturation, reaction enthalpies, driving force of different processes, etc.) are obtained.

Figures 7.3–7.5 illustrate results from equilibrium calculations. Figure 7.3 shows the change in equilibrium composition when SiH_4 is added to a H_2/WF_6 gas mixture. *CVD phase diagrams*

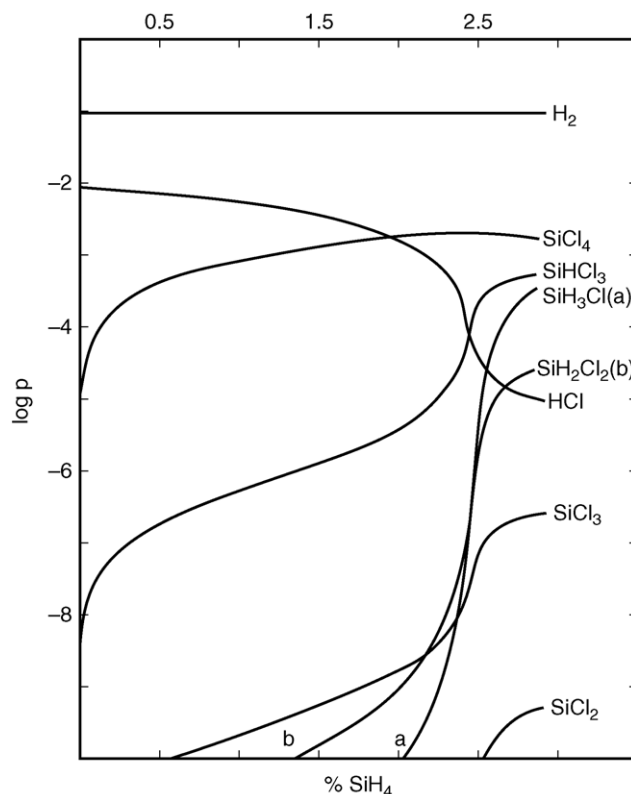


Figure 7.3: Partial pressures of vapor species in the homogeneous reaction between H_2 , WF_6 and SiH_4 . Total pressure = 0.1 torr, temperature = 300 °C, $\text{H}_2/\text{WF}_6 = 30$ [10].

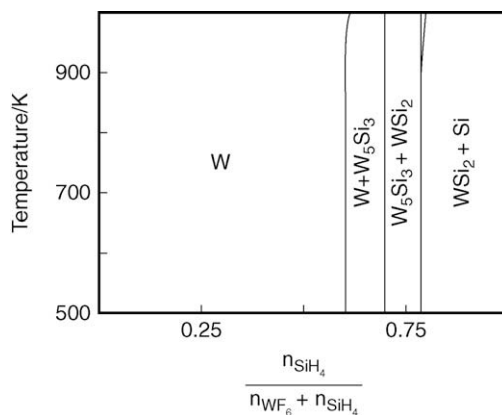


Figure 7.4: Calculated CVD phase diagram for the W– Si system. Reactants WF_6 , SiH_4 and H_2 , total pressure = 0.1 torr, $\text{H}_2/\text{WF}_6 = 39$ [10].

are constructed to provide an overview of experimental conditions used in depositing a certain thin film material [11]. Figures 7.4 and 7.5 are examples of calculated CVD phase diagrams. The number of variables required to construct a complete CVD phase diagram is given by the phase rule. Normally various sections (constant temperature, constant total pressure, constant molar ratio between two of the reactants, while varying the number of moles of a third reactant) are used. Finally, for more theoretical work, *predominance diagrams* with element chemical potentials as variables are employed. In these diagrams, the phase stability ranges are limited by straight lines.

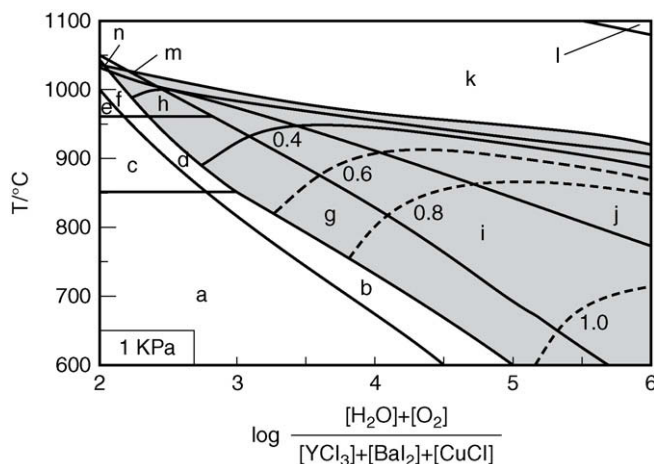


Figure 7.5: Calculated CVD phase diagram for deposition of high-temperature superconductor $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$. Gray-shaded stability regions contain the superconducting phase. Contour lines represent the yield of $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$. Precursors YCl_3 , BaI_2 and CuCl , O_2 , and H_2O , molar ratios $\text{YCl}_3:\text{BaI}_2:\text{CuCl} = 1:2:3$, $\text{O}_2:\text{H}_2\text{O} = 1:1$, total pressure 1 kPa [13].

The reliability of the equilibrium computations described above is dependent on the availability and accuracy of thermochemical data as well as the identification of all substances – vapor species and condensed phases – that are of importance in the system. Examples of sources of thermochemical data are given in [12–14]. In cases where data do not exist or the data are unsatisfactory or unreliable, estimation procedures can be used [e.g. 13]. Finally, a few references illustrating the use of thermodynamic computations in CVD have been selected [15–24].

7.3.3 Adhesion

Production of adherent coatings with desired properties is the ultimate goal of all CVD work. There are, however, several factors which degrade adhesion between the coating and the substrate.

Stress can be introduced as intrinsic stress (due to deposition conditions) or resulting from a mismatch in thermal expansion coefficients between the substrate and the coating when cooling down after deposition. Stress can be reduced to a certain extent by depositing a ductile buffer layer prior to the final CVD process. Total stress can also be reduced by decreasing the thickness of the coating as well as by changing the grain size and morphology of the coating.

Homogeneous nucleation in the vapor produces a flaky/powdery deposit. By reducing the degree of supersaturation or the driving force of the process, homogeneous nucleation can be eliminated.

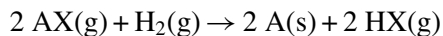
Intermetallic compounds formed at the coating/substrate interface may be brittle, leading to the formation of cracks. The likelihood of crack formation increases with increasing thickness of the layer containing the intermetallic compounds. Deposition of a buffer layer may also improve adhesion in this case.

Hydriding of the substrate may cause poor adhesion. Hydrogen is frequently used in the cleaning procedure prior to deposition. Some metals/alloys can absorb a considerable amount of hydrogen. If the deposition process is run at a temperature at which hydrogen is liberated, the coating will crack and lose adhesion. Hydriding can be eliminated by using other cleaning procedures or by heating the substrate in vacuum or an inert gas after cleaning in hydrogen.

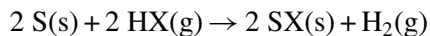
Pores at the coating/substrate interface reduce the adhesion not only because of the fewer bonds at the interface but also because they act as crack initiators. Pores can originate from the coalescence step at the beginning of the CVD process as well as from Kirkendal diffusion (differences in diffusion fluxes of the atoms over the coating/substrate interface).

Oxide films or other surface contaminants can reduce adhesion. A proper cleaning procedure will usually solve this problem.

Chemical attack on the substrate by the reaction products formed during the CVD process (HCl for example) can cause poor adhesion. Chemical attack of the substrate can occur as long as the substrate is exposed to the vapor and is described in the following reactions:



Volatile reaction product HX reacts with the substrate S according to the reaction



Solid substance SX formed may cause poor adhesion. The above reaction can be predicted from thermodynamics.

7.3.4 Substrate Cleaning Procedures

A clean substrate surface free from oxides and other contaminants is critical for good adhesion. The cleaning procedure depends on the substrate used, the material to be deposited, the CVD process, etc. Examples of cleaning techniques are given below. Refer to [Chapter 3](#) for detailed substrate cleaning procedures. Before substrates are placed in the reactor, pickling, grit blasting, etching, degreasing, etc., are carried out. In the CVD reactor surfaces containing hydrogen-reducible oxides, e.g. tungsten oxides, are heated in a hydrogen gas flow at temperatures above the deposition temperature. Metals forming volatile oxides are cleaned by heating in an inert atmosphere. Finally, the heating operations in the cleaning step remove dust particles from the surface, in some cases by the formation of carbides at the surface. After the cleaning procedure the reactor is purged with an inert gas/hydrogen before the deposition process (interlayers or final coating).

7.3.5 The CVD System

Choice of the CVD system is determined by a number of factors:

- reactants used in the process
- maximum acceptable leak rate for air into the system
- purity of the deposit
- size and shape of the substrate
- process economy.

In the following sections, general comments on the design of CVD systems are given.

A CVD system is constructed in three modules:

- reaction gas dispensing system
- reactor, including components for defining gas flows
- exhaust system containing a total pressure controller, vacuum pump, scrubber/or reactant recycling system.

7.3.5.1 Gas Dispensing System

Reactants, which are gases at room temperature, are stored in gas bottles. After pressure regulation, their flows are measured with, for instance, mass flow meters. Use of mass flow meters yields high accuracy and allows microprocessor control of gas flows.

Liquids or solid reactants at room temperature must be fed to the system in other ways (Figure 7.6). They can be admitted into the system by simply heating them above the boiling or sublimation point. The evaporation rate can be varied by varying the source temperature and/or the dimensions of the capillary from the sources. Another way of introducing these substances is to use an evaporator or sublimator and a carrier gas. When an evaporator is used, the carrier gas is bubbled through the liquid to be evaporated or flowed over its surface. The carrier gas picks up the liquid material and transports it into the reactor. Evaporation rate depends on temperature of the liquid, liquid level in the container, and flow rate of the carrier gas. For best possible reproducibility it is important to have a constant level of the liquid in the container. However, some alternatives to these evaporators exist which use carrier gases and are independent of the liquid level. In one alternative, the liquid is evaporated from a vessel, cooled and condensed in a chiller, leaving the carrier gas saturated at the temperature of the chiller. If two or more reactant liquids are used in the process, it is seldom possible to vaporize them in the same evaporator while maintaining the predetermined molar ratio since they normally have different vapor pressures.

The principle of the sublimator is similar to that of the evaporator, in which the material is transferred to the vapor by sublimation (solid $\sim$ gas) and then transported to the reactor by carrier gas.

Non-gaseous reactants at room temperature can also be introduced into the reactor by generating them in situ in the gas dispensing system. If, for instance, the halide AlCl_3 is used in a process, the generator is filled with aluminum sponge. Aluminum chloride is then obtained by passing hydrogen chloride through the generator. Generator variables are temperature, flow rate, and concentration of the hydrogen chloride (varied by dilution with an inert gas).

Direct metering of liquids/solids followed by immediate vaporization in a vessel can also be used. Flow meters and various dispensing pumps are available for metering liquids. The final

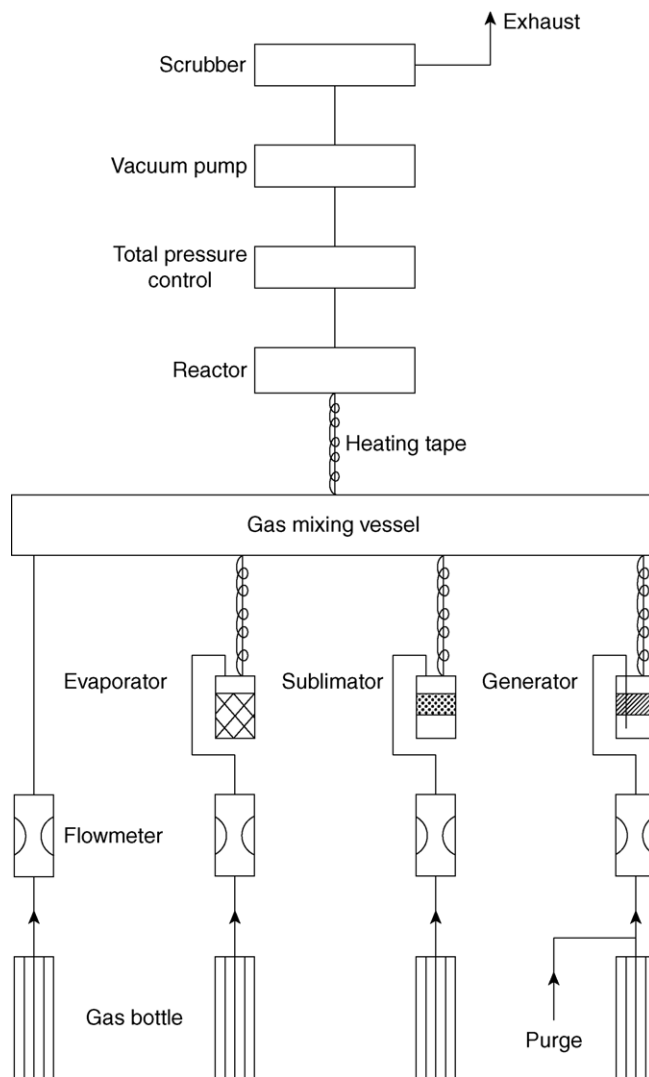


Figure 7.6: Sketch of a CVD system.

vaporization takes place in, for instance, a flash vaporizer [25], a vessel containing pieces of high-temperature porcelain.

Many CVD processes are strongly degraded by contaminants in the vapor. Contaminants originate from the reactants themselves and from various chemical reactions between the gases and the materials in the gas dispensing system (in the tubes, evaporators, sublimators) and from air leakage. The contamination level can be reduced by:

- purifying the reactants: hydrogen and argon can be purified to a level of 1 ppm in commercially available purifiers
- a low leak rate
- using carrier gases which are non-reactive with the materials to be vaporized (in evaporators and sublimators)
- using materials in tubes, vaporizers, reactors, etc., which are compatible with the gases used
- using degassed O-rings that are used as vacuum seals
- installing purge lines, which is important when reactive gases, e.g. halides, are used.

Finally, explosive, flammable and toxic gases (hydrogen, silane, phosphine, arsine) are frequently used in CVD processes. Correct handling of the gases is critical for safety, and every precaution should be taken. Effective ventilation systems and gas detectors (commercially available) should also be used.

7.3.5.2 Reactor

The process selected and the size, shape, and number of substrates define the type of reactor and its geometry. Two main reactor types can be distinguished:

- In a *hot wall reactor* (Figure 7.7), the reactor tube is surrounded by a tube furnace. As a result, the substrates and walls of the reactor all have the same temperature. In addition to the film growth occurring on the substrates, film growth is likely to occur on the inside of the reactor walls. With thicker films on reactor walls, there is a risk that particles will break loose and fall down on the surface of the growing film; thus introducing pinholes. A reaction between the material in the reactor wall and the vapor may also be a source of contamination in this reactor type. Homogeneous reactions affecting the deposition reactions and hence the structure of the films may also take place in the vapor. There is a successive depletion of the reactants as they are

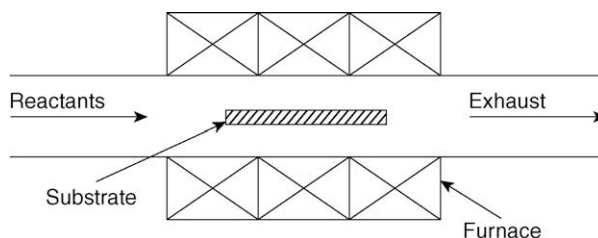


Figure 7.7: Hot wall CVD reactor.

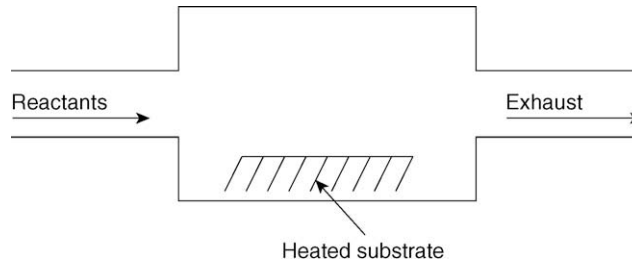


Figure 7.8: Cold wall CVD reactor.

transported through the reactor. Such a depletion may yield different deposition conditions and compositions within the reactor. Finally, many compositions can be deposited simultaneously.

- The walls of a *cold wall reactor* (Figure 7.8) are unheated and, as a result, no deposition occurs on the walls, eliminating the risk of particles breaking loose from the walls. Furthermore, a low wall temperature reduces the risk of contaminating vapor/wall reactions. In this type of reactor, homogenous reactions in the vapor are suppressed and the importance of the surface reactions is increased. Steep temperature gradients near the substrate surface can potentially introduce severe natural convections resulting in a non-uniform film thickness and microstructure. However, there is a tendency to use cold wall reactors frequently in microelectronics owing to their higher flexibility, high cleanliness, high deposition rates (resulting in high wafer throughput), high cooling rates combined with the needs of thickness uniformity, automatic wafer handling, and use of increasing wafer diameter.

Various techniques exist for heating the substrates [27]. Conductive substrates can be heated resistively or by radiofrequency induction. Non-conductive substrates are normally heated by optical techniques (tungsten filament lamps, lasers), thermal radiation techniques, or by susceptors and radiofrequency induction heating. Examples of reactors are shown in Figure 7.9. Fluidized bed techniques can be used for coating a large number of small pieces [26].

To illustrate how the choice of reactor depends on the substrate to be coated, an example of applying a coating inside a tube is given. In this case the tube itself is the reactor. The reactants are introduced in the tube and transported to the heated zone where the deposition occurs. Induction heating as well as tubular furnace heating can be employed. By moving the tube or the heating sources continuously, a coating with uniform thickness can be produced [e.g. 28].

Arrangement of gas flows as well as gas flow rate are of highest importance for obtaining good coatings. Gas flow dynamics are discussed in Section 7.4.

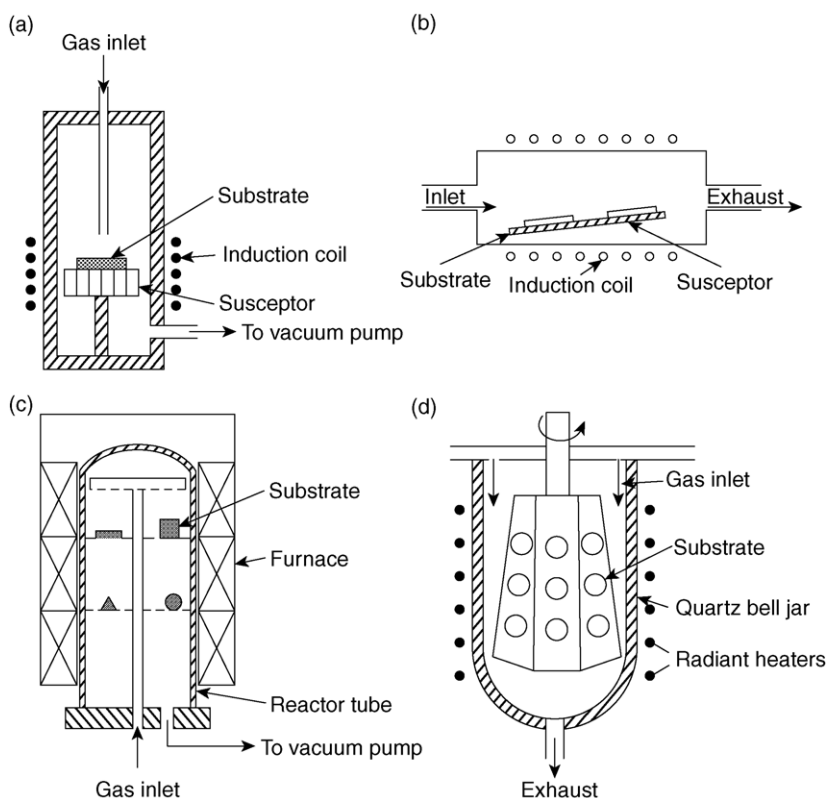


Figure 7.9: Examples of some CVD reactors: (a, b) RF heated cold wall reactors; (c) vertical hot wall reactor; (d) barrel reactor.

7.3.5.3 Exhaust System

The exhaust system contains a vacuum pump, total pressure control, scrubbers, and a recycling system (if used). Processes working at atmospheric pressure do not require vacuum pumps and total pressure control. At reduced pressures, however, pumps as well as some kind of total pressure control must be used.

The choice of the vacuum pump depends on the process (pumping capacity required, pressure range to be used, gases to be pumped). At higher process pressures (> 30 torr), water ring pumps and various mechanical *chemical pumps* are used. Chemical pumps are also employed at lower pressures (1 torr), and at the lowest pressures in combination with, for example, mechanical boosters. When mechanical pumps are used in CVD processes, the pump oil can polymerize or be damaged/contaminated in other ways by certain gaseous species. Pump oil should be chosen with respect to its compatibility with the specific gaseous species. Polymerization of oil can readily be tracked by measuring its viscosity at different times.

Mechanical pumps also produce back-diffusion of oil molecules into the system. Back-diffusion can be held in a trap (zeolite trap, liquid nitrogen cold trap) placed above the pump. With the current trend for using lower pressures to create abrupt interfaces and superlattices, diffusion (to pump hydrogen) and turbo pumps are also utilized. Finally, external oil filtering systems reduce wear in mechanical pumps in processes where solid particles are formed and transported in the vapor to the pump.

In a CVD process, toxic, explosive, and corrosive gases are generally used and formed. Scrubbers are used to remove them before exhaust. Scrubber type must be appropriate to the CVD process used. Halides can easily be neutralized in a water scrubber. Carbon monoxide and hydrogen can be burned in a flame, and arsine can be removed by simply heating the reactor gas in a furnace especially designed for this purpose (i.e. with a high efficiency for stripping arsenic from the gas stream).

Recycling is frequently used to reduce process costs, and becomes necessary in large-scale processes in which expensive reactants are utilized and conversion efficiency of the reactants is low. Techniques for recycling are process dependent. Simple recycling can be achieved in some processes by selective condensation, which can be easily applied in systems where the component to be recycled has the highest boiling point. In the production of boron fibers for example, where hydrogen and boron trichloride are used, unconverted boron trichloride is condensed in the exit stream from the reactor, while the hydrogen and the hydrogen chloride (formed in the process) are not condensed.

7.3.5.4 Analysis of the Vapor in a CVD Reactor

Various spectroscopic techniques can be used to analyze the vapor in a CVD reactor. The purpose of these analyses is to achieve a better understanding of the chemical species in the process. Spectroscopic techniques are also used for process control. Mass, Raman, and infrared spectroscopy are used most extensively [29–33].

7.4 Gas Flow Dynamics

The rate and arrangement of gas flows in a CVD reactor influence deposition conditions considerably. Some fundamentals of gas flow dynamics are given in this section. For further details the reader is referred to textbooks in chemical engineering or other books treating transport processes.

A variety of different states can be present in a gas. In the molecular state, the mean free path of the molecules is much longer than the dimensions of the vessel. In the viscous state, the mean free path is much shorter than the vessel dimensions. The viscous state can be divided into two flow regimes: (1) laminar flow regime where gas velocity is low and the flowing gas layers are parallel, and (2) turbulent flow which occurs at higher velocities. The demarcation

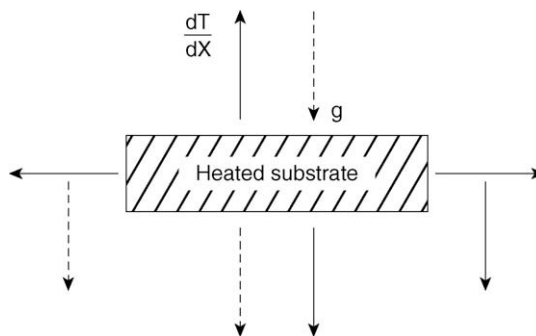


Figure 7.10: Forces near a heated substrate surface. g : gravitational force; dT/dx : temperature gradient.

between laminar and turbulent flow is defined as the value of Reynold's number, Re :

$$Re = \frac{\rho V D}{\eta}$$

where ρ = density of the gas, V = velocity, η = viscosity, and D = diameter of the tube.

Flow is laminar for $Re < 1100$, while for $Re > 2100$ flow is turbulent. The range 1100–2100 is a mixed flow regime.

The Reynold's number characterizes flow in an isothermal environment. In a non-isothermal environment that exists in a cold wall reactor, natural convection produces turbulence even at low flow rates. Consider the region above a heated surface shown in Figure 7.10. For small temperature gradients dT/dx , the density variation of the gas along the coordinate x is compensated by the gravitational field and no movement of the gas occurs. For larger dT/dx , the gas starts to move and laminar flow can no longer be sustained. From Figure 7.10 it can be understood that turbulence above a heated substrate surface can occur at different regions. For example, when the dT/dx is perpendicular to the gravitational field, turbulence occurs at smaller temperature gradients than in the antiparallel case.

Different dimensionless quantities are used to identify conditions of laminar and turbulent flow at different geometries. The Rayleigh number, Ra , and the Grashof number, Gr , define these flow regimes [32]. Ra is simply the product of Gr and the Prandtl number (nearly equal to one for gases).

Diagrams like those shown in Figure 7.11, depicting flow stability regions, are constructed for different geometries and reaction gas mixtures in order to summarize flow. In an isothermal environment, Gr is equal to zero and Re describes the situation completely. In a non-isothermal environment Gr is greater than zero (increases with increasing DT). Turbulence occurs at a specific value of Gr , depending on flow rate of the specific gas mixture and temperature difference between the hot and cold parts of the reactor.

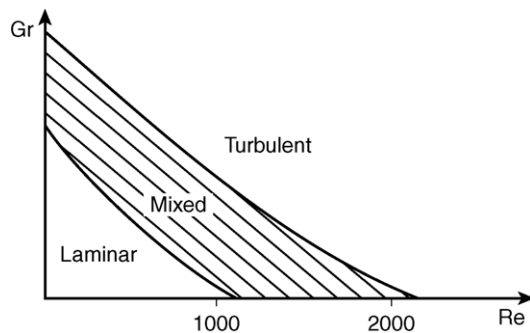


Figure 7.11: Diagram showing flow stability regions.

The laminar flow region is typically used in most CVD processes. High flow rates (turbulence) usually decrease conversion efficiency of the reactants to deposit the coating and very large gas volumes have to be handled. The flow environment around the object to be coated can be visualized as a smoke experiment where smoke is generated inside the reactor from, for example, titanium tetrachloride and water.

7.4.1 Gas Flow Patterns

Gas flow patterns are of greatest importance for growth of films with uniform thickness and composition, particularly at 'high' pressures (about 1 atm). The diffusivity of the vapor species increases at reduced pressures, which results in better mixing of the process gases, and hence the flow fields become less important.

Gas flow patterns are very complicated in many CVD reactors with complex geometries because flow is driven by both pressure differences (forced convection) and gravity (free convection). Free convection contributes to the gas flow pattern not only in cold wall reactors with their steep temperature gradients but also in hot wall reactors with small axial temperature gradients. Free convection is employed for correction of the successive depletion of the reactants in the vapor as they flow through the reactor. Fluid flow phenomena characteristic of various CVD reactors have been reviewed by Westphal [33] and Jensen [34].

In gas flow calculations the continuity equation for the total mass for single components, energy and momentum must be solved. For a suitable choice of experimental conditions (flow regimes and reactor geometries) simplifying equations and boundary conditions, resulting in reasonable computer times, are obtained. As an introduction, results from detailed flow calculations for two main reactor types are summarized. Wahl [35] calculated flow fields in several cold wall reactors for the laminar flow region (atmospheric pressure) for CVD of silicon nitride from SiH_4 and N_2 . The reactor geometry is shown in Figure 7.12. Flow patterns calculated for this geometry and the inverted geometry (difference in the buoyance-driven

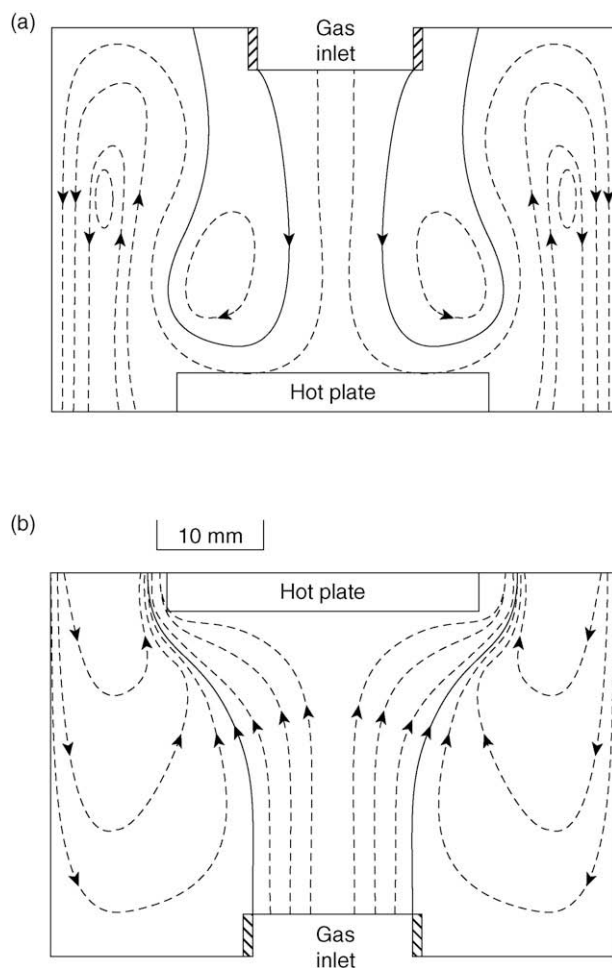


Figure 7.12: Gas flow pattern in a cold wall reactor, where the forced and buoyance-driven convection (a) interact, and (b) counteract, substrate temperature 900 K, $Re = 50$ [35].

convection) are shown in Figure 7.12. The flow pattern becomes more complicated for the inverted geometry, i.e. when forced convection and gravity interact. The flow pattern, including generation of loops and rolls, is strongly dependent on the ratio of the free convection and forced convection.

To demonstrate the influence of the reactor geometry on the flow pattern, a calculation of Wahl and Hoffman [36] will be used as an example. The reactor geometry considered as well as the results from the calculations are shown in Figure 7.13. The flow pattern in this geometry is not as complicated as that obtained in the previous geometry (Figure 7.12), where the diameter of the inlet gas tube was half the diameter of the hot plate.

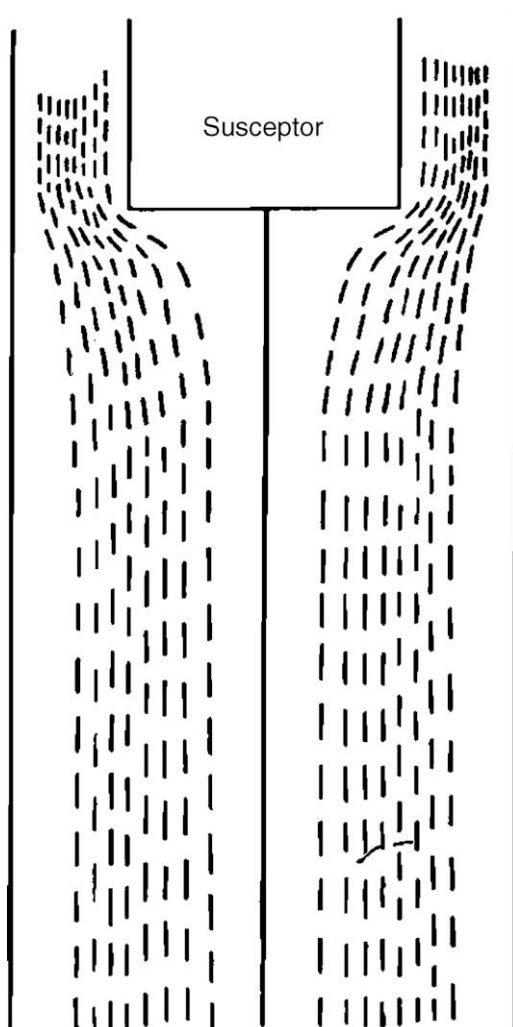


Figure 7.13: Gas flow pattern in a cold wall reactor with geometry different than that shown in Figure 12 [36].

A technique frequently used for correction of the successive depletion of the reactants as they are transported through a hot wall reactor is the application of a temperature gradient in the axial (flow) direction of the reactor. Even small temperature gradients, however, can induce buoyancy-driven convection. The flow pattern in a hot wall reactor with a temperature gradient for the atmospheric CVD of GaAs in the Ga–AsCl₃–H₂ system was calculated for different temperature gradients, gas flow velocities, and reactor heights by Westphal [33]. A typical result from their calculations is shown in Figure 7.14. It can be seen that a convection roll, induced by free convection, is generated. The effect of free convection on the gas flow pattern

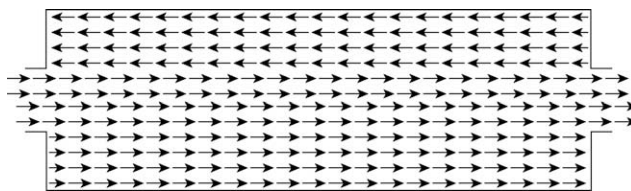


Figure 7.14: Gas flow pattern in a hot wall reactor with a temperature gradient of 6 K/cm, linear gas flow velocity of 2 cm/s, and channel height 5 cm, for deposition system Ga-AsCl₃-H₂ [33].

decreased with decreasing temperature gradients, increasing gas flow velocities and decreasing reactor heights. No extreme conditions were required to generate the convection rolls shown. They were obtained at a temperature gradient of 6 K/cm, gas flow velocity of 2 cm/s and reactor height of 5 cm.

Convection rolls are frequently generated in CVD, and can cause dilution of the reaction gas with reaction products, resulting in an alteration of the deposition conditions. Resultant rolls may cause problems for multilayer growth with well-defined phase boundaries and for the creation of sharp doping profiles. These problems can be solved by using extreme low total pressures (in the 10^{-3} torr range).

7.4.2 Boundary Layers

In CVD the substrates are immersed in a gas stream. From fluid mechanics it is known [37] that boundary layers are developed near the substrate surface. Boundary layers are defined as the region near the substrate surface where gas stream velocity, concentration of the vapor species and temperature are not equal to the same parameters in the main gas stream. Thus, a velocity boundary layer, concentration boundary layer and thermal boundary layer develop. The development of a velocity boundary layer in a laminar flow region is sketched in Figure 7.15. Gas velocity is zero at the substrate surface and increases to a constant value (the bulk gas flow velocity). The boundary layer is the layer over which the gas flow velocity changes.

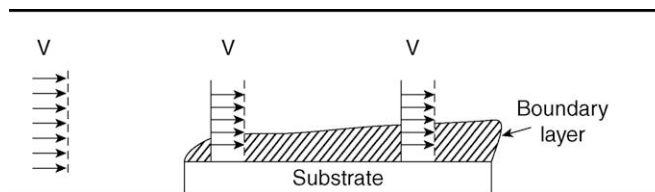


Figure 7.15: Definition of the velocity boundary layer.

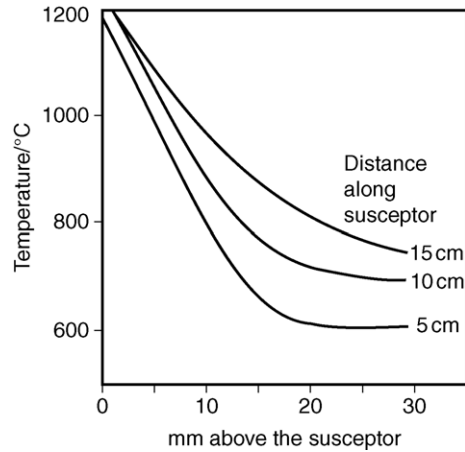


Figure 7.16: Temperature profile in He. Linear gas flow velocity: 24.9 cm/s [29].

The thickness δ of the boundary layer (laminar flow) at a position X on the substrate or susceptor [37] is given by

$$\delta = a(\eta X / \rho V)^{1/2}$$

where a is a proportionality constant, η is the viscosity of the gas, v is the velocity of the gas, and ρ is the density of the gas. From knowledge of the temperature and pressure dependence of η , v , and ρ [32, 37] it is deduced that the thickness of the boundary layer increases with increasing temperature and decreasing total pressure. Moreover, thickness also increases with increasing transport distance of the gases along the substrate surface.

Development of boundary layers in CVD processes has been investigated both experimentally and theoretically. Eversteijn et al. [38] used smoke experiments to visualize the flow pattern in a horizontal epitaxial reactor. Smoke was generated from TiCl_4 and H_2O . They observed an immobile layer of gas, called the stagnant boundary layer, above the susceptor. It was shown later, however, that in steep temperature gradients (near the susceptor) fine particles are driven away from the susceptor by thermophoretic forces [39]. This demonstrated that smoke experiments can only be used to map flow at large distances from a heated susceptor.

Ban and Gilbert [29] investigated heat transport in a cold wall reactor by heating a susceptor in helium and measuring the temperature at different locations above it with a small diameter thermocouple. The very steep temperature gradient is apparent in Figure 7.16.

Ban and Gilbert also investigated concentration profiles of various vapor species in silicon CVD from H_2/SiCl_4 gas mixtures. They introduced a fine capillary probe attached to a mass spectrometer at different locations above the susceptor. The concentration profile of SiCl_4 and reaction product HCl can be seen in Figure 7.17. The thickness of the concentration boundary

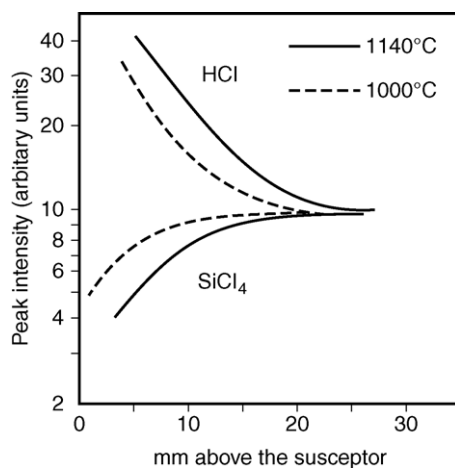


Figure 7.17: Concentration profiles of SiCl_4 and HCl in the CVD of silicon from SiCl_4 and H_2 . Transport distance along the susceptor: 12.5 cm; linear gas flow velocity: 24.9 cm s^{-1} , - - - 1000°C , - 1140°C [29].

layer in this case is greater than 2 cm. Successive depletion with respect to the reactants as they were transported through the reactor is shown in Figure 7.18. At a height of 7 mm above the susceptor and 15 cm downstream of the susceptor, partial pressure of SiCl_4 was reduced to $\sim 50\%$ of the initial value. Sedgwick et al. [30] measured temperature and concentration

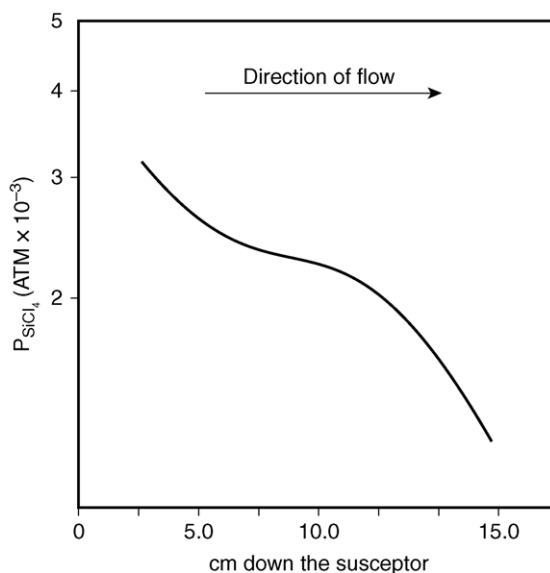


Figure 7.18: Partial pressure profile of SiCl_4 as a function of the transport distance along the susceptor at a height of 7 mm above the susceptor [29].

profiles in an air-cooled horizontal cold wall reactor using Raman scattering. They observed a steep temperature gradient near the susceptor. The temperature profile developed was dependent on the position along the susceptor.

Giling [40] investigated gas flow patterns and temperature profiles at atmospheric pressure in air-cooled and water-cooled horizontal epitaxial reactors using interference holography. H_2 , He, N_2 , and Ar gases were used. H_2 and He yielded stable laminar flows through both the water-cooled and the air-cooled reactors. At flow velocities higher than 40 cm s^{-1} a cold gas finger, indicating incompletely developed flow and temperature profiles, was observed in the air-cooled reactor. N_2 and Ar behaved quite differently from H_2 and He, and as a result, different convective effects were observed. At flow velocities greater than 4 cm s^{-1} , a laminar layer about 8 mm thick developed near the susceptor, while the gas above this layer appeared to be in turbulence.

Giling also pointed out the importance of entrance effects, i.e. that it takes a specific distance (the entrance length) from the susceptor edge for full velocity and temperature profiles to develop. According to Schlichting [37], the entrance length for development of a full velocity profile is given by the equation

$$X = 0.04hR_e$$

where h is the height of the channel. Hwang and Cheng [41] predicted that the thermal entrance length was seven times larger than the flow entrance length. Giling's measurements confirmed this for H_2 .

Coltrin et al. [42] developed a mathematical model for silicon CVD from silane in a cold wall reactor. The model includes gas-phase chemistry as well as fluid mechanics and predicts temperature, velocity, and concentration profiles for many vapor species. Figure 7.19 depicts the temperature contour for a typical calculation. The thickness of the boundary layer is in the centimeter range and increases with increasing gas transport distance along the susceptor.

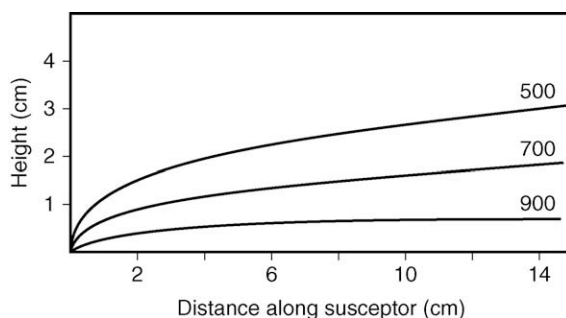
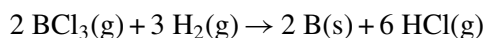


Figure 7.19: Calculated temperature contours for silicon CVD from silane (0.6 torr) and helium as a carrier gas (600 torr). Temperature: 1018 K; gas flow velocity: 15.3 cm s^{-1} [42].

7.4.3 Mass Transport Processes Across a Boundary Layer

Four mass transport processes across a boundary layer can be distinguished:

- Fickian diffusion occurs from a concentration gradient across the boundary layer.
- Thermal diffusion or Soret diffusion is induced by a temperature gradient in, for example, a cold wall reactor [32]. This type of diffusion is most important in systems having large differences in molecular weights and molecular size between vapor species.
- A concentration gradient leads to a density gradient, resulting in a buoyancy-driven *advective flux* [42].
- In the overall CVD reaction, the number of moles of gas may be changed. This creates flux (Stefan flux) towards or away from the substrate surface. In, for example, the CVD of boron from BCl_3 and H_2 according to the reaction



the number of moles in the vapor is changed from 5 to 6, causing a flux from the substrate [43].

7.5 Rate-Limiting Steps During CVD

Various sequential process steps occur in CVD. Each of these steps can be rate limiting in the absence of thermodynamic limitations. Plausible rate-limiting steps are as follows (see also Figure 7.20): (a) transport of gaseous reactants to the boundary layer surrounding the substrate (free and forced convection); (b) transport of gaseous reactants across the boundary layer to the surface of the substrate (diffusion and convections flows); (c) adsorption of reactants on the surface of the substrate; (d) chemical reactions (surface reactions between adsorbed species, between adsorbed species and reactants in the vapor and or between reactants in the vapor), (e) nucleation (at least at the initial stage); (f) desorption of some of the reaction products from the

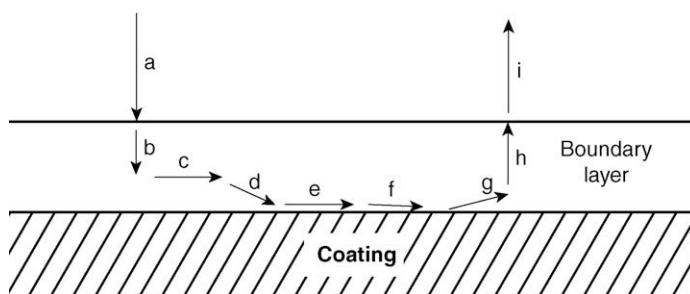


Figure 7.20: The various steps in a CVD process.

surface of the substrate; (g) transport of reaction products across the boundary layer to the bulk gas mixture; (h) transport of reaction products away from the boundary layer. In each of these steps several processes may proceed simultaneously.

Even though several rate-limiting steps can be identified in a CVD process, only five main categories of control are normally discussed:

- *Thermodynamic control* implies that the deposition rate is equal to the mass input rate into the reactor (corrected for the yield of the process). This occurs at extreme deposition conditions (very low flow rates, high temperatures, etc.). Temperature dependence of the deposition rate is obtained from thermodynamic calculations.
- *Surface kinetics control* or nucleation control exist if the deposition rate is lower than the mass input rate into the reactor and the mass transport rate in the vapor to or from the substrate. Surface kinetics control is favorable for obtaining coatings of uniform thicknesses on substrates with complex shapes. Mechanisms of surface reactions are discussed in Section 7.6.
- *Mass transport control* is used to control a process in the vapor in the reactor or from the substrate surface. This occurs frequently at high pressures and high temperatures.
- *Nucleation control*. At low supersaturation the deposition rate may be controlled by the nucleation.
- *Homogeneous reaction control*. In some processes the formation rate of key species in the vapor may control the deposition rate.

Since mass transport in the vapor or surface kinetics usually controls the deposition rate, the following discussion is limited to only these two cases. Surface kinetics control is normally desirable and results in a maximum throwing power or optimum step coverage. Figure 7.21 shows conditions of complete mass transport control, complete surface kinetics control and mixed control. In the surface kinetics control regime, fast diffusion in the vapor is combined with slow surface reaction. For mass transport control, surface kinetics is fast while mass transport in the vapor is slow.

Reaction resistances are often used to predict rate-limiting steps or control in CVD. To illustrate their principle use, reaction resistances are employed to define the surface reaction control and the mass transport control, respectively.

Diffusion flux J_D across the boundary layer is given by

$$J_D = \frac{D}{RT} \frac{P_b - P_s}{\delta}$$

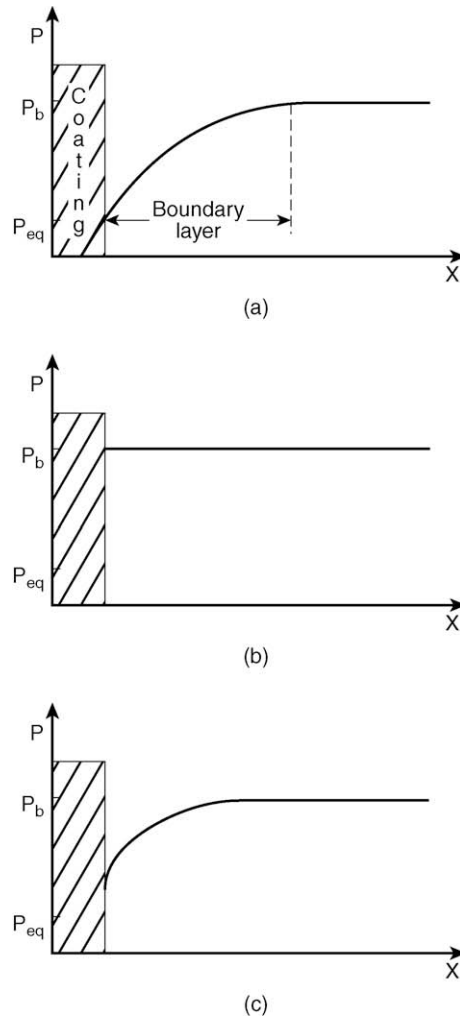


Figure 7.21: Diagrams illustrating examples of complete mass transport control in the vapor (a) and surface kinetics control (b), respectively; (c) shows conditions of mixed control.

where D = diffusion coefficient, R = gas constant, T = absolute temperature (K), b = boundary layer thickness; P_b and P_s : see Figure 7.21.

Mass flux J_M towards the surface is expressed as

$$J_M = \frac{k_m}{RT} (P_s - P_{eq})$$

where k_m is the mass transfer coefficient.

P_b and P_{eq} are derived from the reaction gas composition and from thermodynamic calculations, respectively. P_s can be eliminated by assuming steady-state conditions ($J_M = J_o$)

$$P_s = \frac{P_b + \frac{k_m \cdot \delta}{D} \cdot P_{eq}}{\frac{k_m \cdot \delta}{D} + 1}$$

J_m is thus given by

$$J_M = \frac{1}{RT} \frac{P_b - P_{eq}}{\frac{\delta}{D} + \frac{1}{k_m}}$$

$P_b - P_{eq}$ is the driving force for the process and δ/D and $1/k_m$ are reaction resistances. If $\delta/D \gg 1/k_m$ the process is controlled by the mass transport in the vapor, while surface reaction control is achieved when $1/k_m \ll b$.

As stated previously, surface kinetics control is a condition prerequisite to obtaining coatings with uniform thickness on complex shaped substrates. Temperature and pressure dependence of the reaction resistances must be analyzed to achieve surface reaction control.

Thickness δ of the boundary layer (laminar flow) at a position x on the substrate is

$$\delta = a \{ \eta x / \rho v \}^{1/2}$$

where a = proportionality constant, η = viscosity of the gas, v = velocity of the gas, and ρ = density of the gas.

The value of ρ depends on both temperature and pressure, while η and v depend only on temperature.

$$\rho = Mp/RT$$

where M = molecular weight and p = total pressure;

$$\eta = \eta_o (T/T_o)^m$$

where T_o = reference temperature, η_o = reference value, m = constant ($0.6 < m < 1.0$), and

$$v = v_o T/T_o$$

where v_o = reference velocity.

From the equations for ρ , η , and v , the pressure and temperature dependence of δ is expressed as

$$\delta = \text{const}(T^{m/2}/p^{1/2})$$

The pressure and temperature dependence of the diffusion coefficient D is

$$D = D_{i,o} (p_i/p)(T/T_o)^{1.75}$$

where $D_{i,o}$ is the reference value of the diffusion coefficient and p_i is the partial pressure of species i . The reaction resistance is then

$$\delta/D = \text{const } p^{1/2}/T^{(1.75-m/2)}$$

Hence δ/D increases with increasing pressure and decreasing temperature.

The value of k_m follows the Arrhenius equation

$$k_m = A \exp^{E_a/RT}$$

where E_a is an activation energy. Thus surface reaction resistance increases with decreasing temperature. This increase is more rapid than the δ/D increase with decreasing temperature. Hence surface reaction control can be achieved at lower temperatures.

The surface reaction control regime should be chosen because it generally possesses the most attractive process conditions (highest throwing power). Conditions for surface kinetics control can be identified from Arrhenius plots (logarithm of the deposition rate versus the reciprocal temperature). In this case, the slope of the Arrhenius plot has a high negative value, often in the range 100–300 kJ/mol. For mass transport control, the slope of the Arrhenius plot can be either positive (exothermic processes) or negative (endothermic processes) (Figure 7.22). When total pressure decreases, the diffusion rate of the species in the vapor increases, indicating that surface kinetics control is readily achieved at low pressures. Figure 7.23 illustrates that the temperature region of surface kinetics control expands at lower pressures.

Surface kinetics can also be attained by increasing the gas flow velocity (Figure 7.24). At low gas flow velocities, the thermodynamics control the deposition. Increasing the gas flow means entering the mass transport controlled regime. The surface kinetics control is reached at even higher gas flow velocities.

The fourth possibility to achieve the surface kinetically controlled region is to use another precursor with a higher thermochemical stability. As shown in Figure 7.25, use of SiCl_4 instead of SiH_4 results in surface kinetics control at higher temperatures.

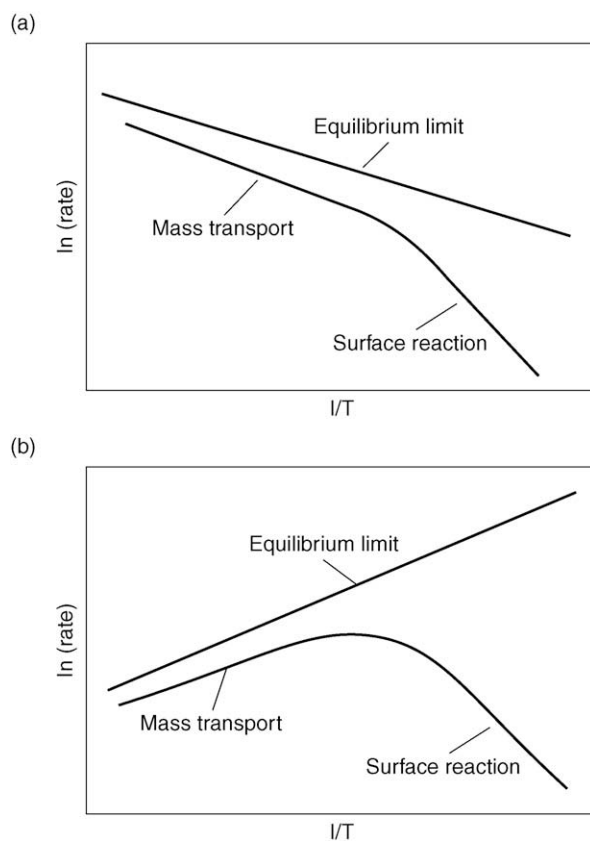


Figure 7.22: Schematic Arrhenius plots for (a) endothermic and (b) exothermic processes.

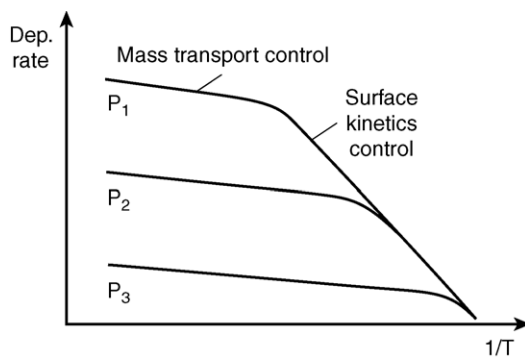


Figure 7.23: Regions of mass transport and surface kinetics control at different total pressures ($P_1 < P_2 < P_3$).

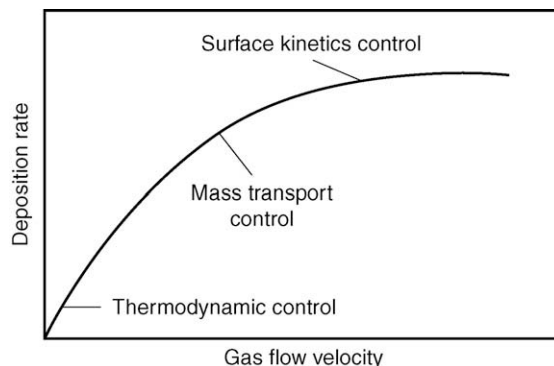


Figure 7.24: Influence of gas flow velocity on the control of a CVD process.

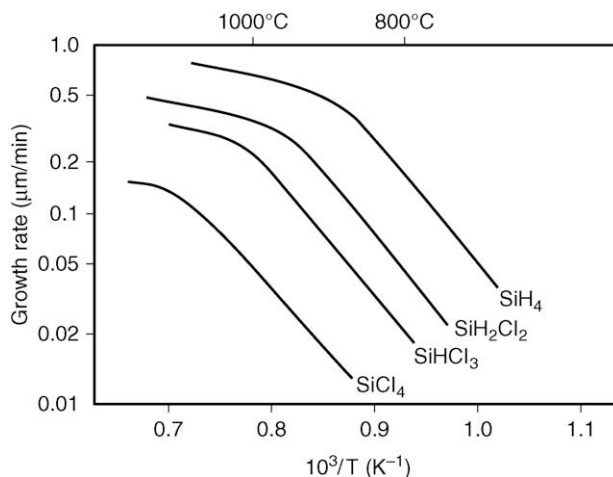
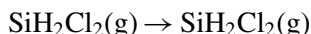


Figure 7.25: Influence of the thermochemical stability of the precursor on the process control at silicon CVD.

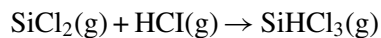
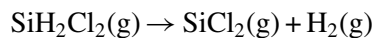
7.6 Reaction Mechanisms

Reaction mechanisms in CVD processes are very complicated and only a few are well known. Reactants are transported to the substrate surface in the deposition process. Molecules and/or atoms are adsorbed on specific surface sites. After surface diffusion, the molecules/atoms are incorporated in a step and finally, after diffusion along the step, incorporation in a stable crystallographic site takes place. The investigation by Bloem and Claassen [45] of CVD rate-determining reactions of silicon from SiH_2Cl_2 in the temperature range 800–1000 °C illustrates the various steps of a CVD process. A list of the reactions considered is given below.

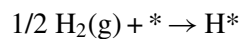
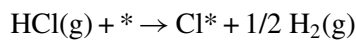
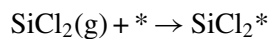
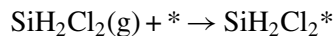
1. Transport of SiH_2Cl_2 across the boundary layer:



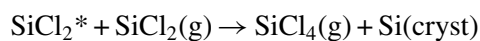
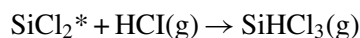
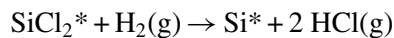
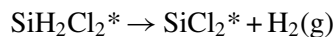
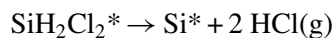
2. Homogeneous reactions in the vapor:



3. Adsorption at free surface sites *:

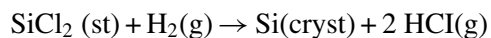
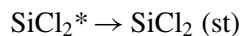
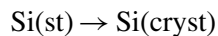
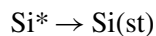


4. Surface reactions:



$\text{Si}(\text{cryst})$ = stable crystallographic site in the crystal grown.

5. Growth reactions; surface step sites are denoted (st):



In CVD of silicon from SiH_2Cl_2 , the last reaction given was rate determining.

7.7 Nucleation

Since the properties of a material are influenced by grain size, defects, inclusions, etc., nucleation is the most important process in the deposition of materials. At the initial stages of growth, nucleation on a foreign substrate determines the grain size in the 'first layer', defects in it and, to a large extent, adhesion. In the subsequent growth secondary nucleation may occur with a generation of new grains, defects, inclusion of vapor species in pores, etc.

The various steps during the heterogeneous nucleation of an element A on a foreign substrate is schematically shown in Figure 7.26, in which hydrogen and AX react. A atoms deposited are adsorbed on the surface of the substrate. Subsequently the adsorbed atoms may desorb from the substrate, diffuse into the substrate, possibly with the formation of intermediate phases, or react with HX with the formation of AX. Unstable aggregates of A atoms, embryos, are formed after surface diffusion and direct impingement of A atoms from the vapor. Some of these embryos will grow at the expense of others and attain the status of stable A nuclei (supercritical A nuclei). A continuous layer is formed after lateral growth and coalescence. The growth rate of the nuclei is determined by the concentration of adatoms. Finally, the coalescence generates, in general, defects, i.e. grain boundaries.

Three-dimensional nucleation typically occurs on foreign substrates. However, when nucleation takes place on native substrates (nucleus and substrate of the same material)

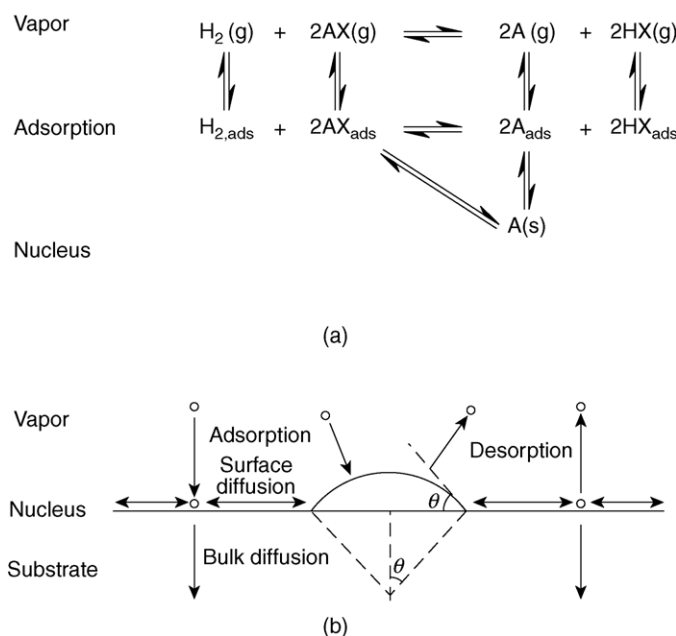


Figure 7.26: Schematic representation of nucleation of A on a substrate during hydrogen reduction of AX (a), and various 'mechanistic pathways' that can be followed by A (b).

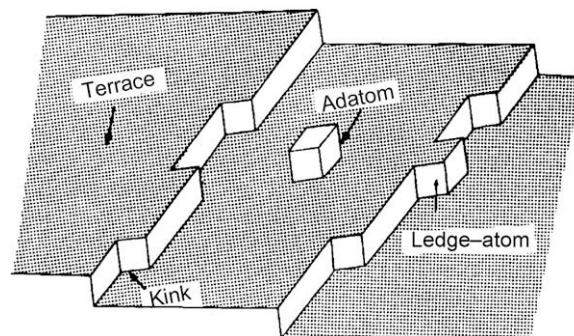


Figure 7.27: The Terrace, Ledge and Kink (TLK) model of a surface.

two-dimensional (2D) nucleation is possible. The TLK model (Terrace, Ledge, Kink) of a surface is used to describe 2D nucleation (Figure 7.27). Besides terraces, ledges, and kinks, atoms adsorbed on the surface (adatoms) exist. Deviation from the equilibrium concentration of the adatoms is a measure on the driving force of the growth process (positive deviation) or of the etching process (negative deviation). Surfaces grow by incorporating surface-diffusing atoms into the steps. This corresponds to a lateral movement of the steps.

The probability of generating new nuclei between the surface steps depends on surface diffusion and deposition rate (the impingement flux of atoms). At a high temperature and a low deposition rate, adatoms have time enough to diffuse and reach the surface steps and be captured by them. A lower temperature and/or higher deposition rate results in shorter diffusion distances, facilitating clustering of adatoms between the steps (2D nucleation). At even lower temperatures and/or higher deposition rates (shorter diffusion distance) amorphous growth occurs [46]. Finally, defects are introduced into the layers when advancing steps meet each other or nuclei.

Surface diffusion is strongly affected by the accessibility of free surface sites. In a CVD process, it is likely that most of the surface sites are occupied by strongly adsorbed molecules. During CVD of silicon from Si-H-Cl gas mixtures, for example, 99% of surface sites are occupied by hydrogen and chlorine atoms [47]. Moreover, impurity adsorption on surface steps can effectively prevent capture of diffusing adatoms. The result is that supersaturation sufficient for nucleation can be built up between surface steps [48]. In summary, layer growth (no nucleation) can only be expected at high temperatures, low deposition rates, and low adsorption. This requires long diffusion distances and the free incorporation of diffusing adatoms at the steps.

The nucleation rate is frequently high ($\sim 10^{10} \text{ cm}^{-2} \text{ s}^{-1}$) after a suitable incubation time. A saturation value of the nucleus density, which remains constant during a relatively long period, is thus achieved (Figure 7.28) [49]. The saturation value is obtained at a stage when the nuclei are so dense that a saturation high enough for nucleation cannot be built up between the nuclei,

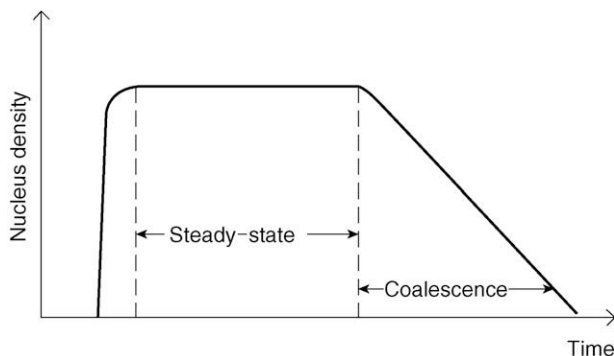


Figure 7.28: Nucleus density as a function of process time.

i.e. when the mean diffusion distance is longer than half the mean nucleus distance. Subsequently, nuclei grow laterally and nucleus density is constant until coalescence occurs. The saturation nucleus density, N_s , is strongly dependent on process conditions. Figure 7.29 shows the influence of temperature on N_s for different silanes for silicon CVD.

Because of high supersaturation possible in CVD, nuclei of critical size consist of only a few atoms. This means that the thermodynamic treatment of nucleation on the basis of microscopic aggregates [51] is not justified. Instead, statistical mechanical methods must be applied [52].

The highest nucleation rate is attained at locations where supersaturation required for nucleation is most rapidly built up. This is assumed to occur at sites having long adatom

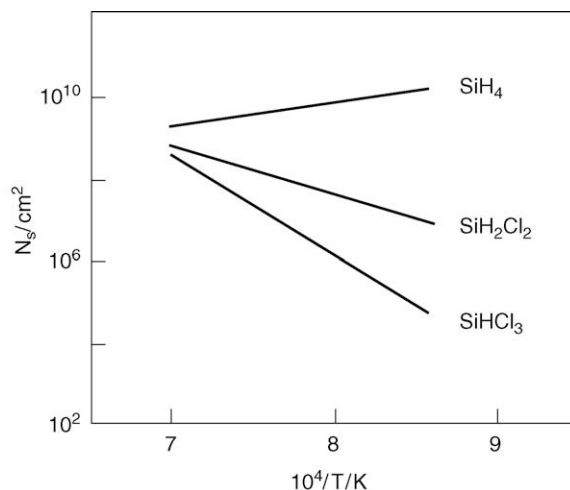


Figure 7.29: Influence of temperature on the saturation nucleus density at silicon CVD from various silanes [50].

residence times and/or at sites of high deposition rate of adatoms. Owing to the long residence time, nucleation on surface steps is highly probable at low deposition rates. Grain boundaries can be favorable diffusion paths, resulting in a high deposition rate of adatoms and hence nucleation of grain boundaries.

Nucleation is strongly affected by surface roughness. An example based on an investigation of preferential nucleation of boron on tungsten filaments illustrates this process. The tungsten filaments used had a rough surface (Figure 7.30a), which originated from the filament drawing process. The ridges on the filament served as nucleation sites (Figure 7.30b). Preferential nucleation on the ridges of the filament is explained as follows [53]. At the onset of the

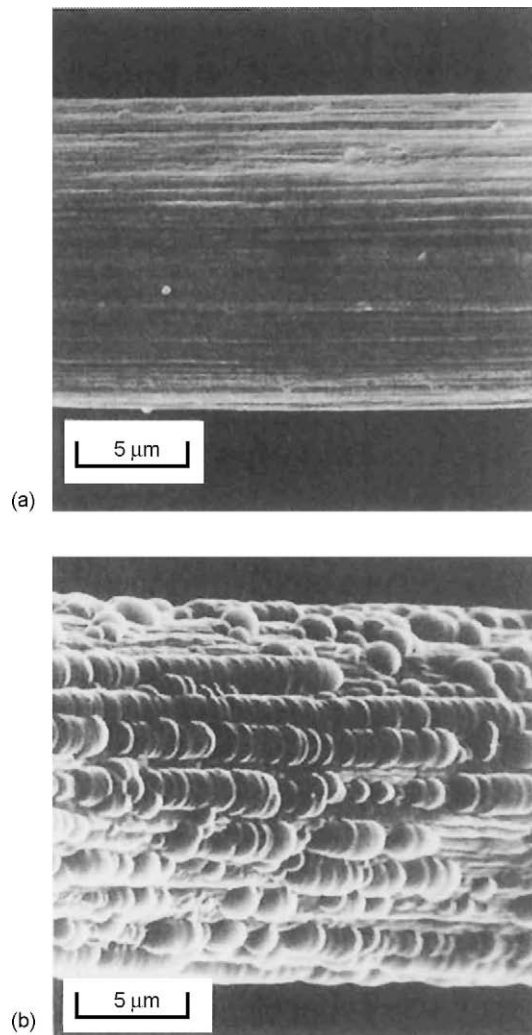


Figure 7.30: (a) Surface of a tungsten filament, and (b) preferentially nucleated boron on ridges of the filament [53].

deposition reaction, boron atoms are added to the substrate surface. Simultaneously, boron is lost from the surface by diffusion into the substrate with the formation of tungsten borides. The diffusion flux, which initially is equal to the deposition rate, later decreases with increasing boride layer thickness (increased diffusion resistance). For geometric reasons it is obvious that the thickness of the boride layer increases at a higher rate under a ridge than under a groove. Consequently, the critical surface concentration for nucleation of boron is reached earlier on a ridge than in a groove.

7.8 Surface Morphology and Microstructure of CVD Materials

Surface morphology and microstructure of CVD materials are controlled by many factors that are often interrelated, such as substrate, temperature, supersaturation, deposition rate, impurities, temperature gradients, and gas flows. In this section a number of theories and classifications of CVD morphologies and microstructures are introduced.

Van den Brekel and Jansen developed and applied a stability theory for single-phase vapor growth [54]. If an arbitrary perturbation at the vapor/solid interface decreases with increased time, the interface is considered stable. However, the interface during CVD in an isothermal condition is unstable. On the other hand, because of the fact that relaxation times in films are much longer than deposition times (a few minutes) smooth layers can be grown even in unstable processes.

The instability of the interface in a vapor growth process can also be described in the same terms as those used to explain dendritic growth from a melt in a negative temperature gradient. Random surface irregularities are frequently formed in growth processes. Surface irregularities have a higher rate of growth if they extend into regions of higher supersaturation. In a CVD process, surface irregularities have better access to fresh reaction gas, which results in a higher supersaturation and hence a higher deposition rate. Also, a negative temperature gradient, as in the cold wall reactor, may result in a higher supersaturation for outgrowths.

Blocher related the various microstructures formed in CVD to temperature and supersaturation process conditions [55]. Epitaxial growth occurs at high temperature/low supersaturation (Figure 7.31). Decreasing temperature/increasing the supersaturation results in the formation of platelets, whiskers, etc. At high supersaturation, a powder resulting from the homogeneous nucleation in the vapor is obtained. Only comments on the growth of selected microstructures are given below.

Epitaxial growth, which is frequently used in the microelectronics industry, occurs at relatively low growth rates. It is affected by the deposit–substrate crystallographic misfit, substrate surface quality, thermal stresses over the substrate, and polycrystalline regions in the substrate. High surface mobility of adsorbed species is required for epitaxial growth, i.e. usually enhanced by a high temperature.

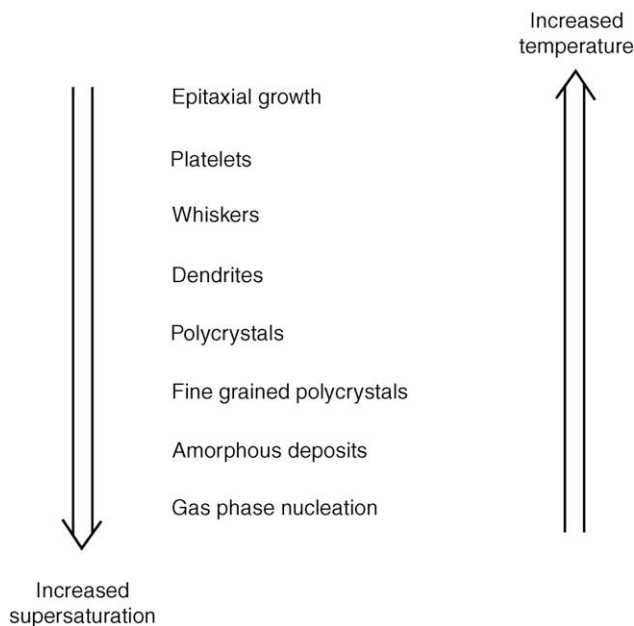


Figure 7.31: Microstructure sequence of CVD materials [55].

Columnar grains are common in CVD films, which can exhibit a high degree of texture. During initial nucleation, nuclei of different crystallographic orientations are formed. Depending on the anisotropy in the growth rate of various crystal surfaces, nuclei will grow at different rates. This preferential growth results in a characteristic columnar growth. Numerous examples of columnar growth in CVD can be found in Proceedings of the International CVD Conference series published by the Electrochemical Society.

Surfaces grow by incorporating surface-diffusing adatoms into surface steps. However, preferential adsorption of molecules at surface steps prevents surface-diffusing adatoms from being captured. Thus a new growth mechanism is required. Throughout the years, the structure of CVD materials has been modified by adding small amounts of foreign substances (growth modifiers) to the reaction gas mixture.

7.9 Selective Deposition

CVD can readily be scaled up to a large-area deposition technique. However, CVD is also well adapted for local deposition or *selective deposition*, where deposition occurs only on specific regions of the substrate surface. Selectivity is achieved by using various focused beams (photons [56], electrons [57–59], or ions [60, 61]). Energetic beams induce local CVD reactions on those areas which are incident. It is also possible to irradiate the substrate surface

through a mask with, for example, a laser [62]. Openings in the mask define the substrate areas where the deposition takes place.

Selective CVD can also be achieved on patterned substrates. Selectivity in this case is based on differences in the initial interfacial reactions between the different substrate materials and vapor. Interfacial reactions on one substrate material should be inhibited completely to avoid nucleation, while deposition reactions should be stimulated on those substrate areas where deposition is required.

Several major categories of selective deposition systems exist. In the system described above, deposition takes place on one substrate material while no deposition takes place on the other. However, different phases can also be deposited simultaneously and selectively on different materials, resulting in phase-selective deposition. Analogous to phase-selective deposition, films of different microstructures or different chemical compositions can be deposited on different substrate materials, and hence selectivity in microstructure or chemical composition is attained.

Selective deposition is an emerging field and the demand is great for these processes in many application areas. With the continuous miniaturization of integrated circuit feature sizes there is a need for self-aligned processes. Examples are selective tungsten metallization in very large scale integration (VLSI) and selective gallium arsenide (GaAs) epitaxy for monolithic integration of optoelectronic devices. Other applications include micronics, heterogeneous catalysis, engineering of film/substrate interfaces, and growth of artificial 2D and 3D materials (e.g. photonic crystals). Since selective deposition on patterned substrates is based on interfacial chemistry, there are practically no restrictions on the dimensions of the deposited material islands. This opens up a fascinating perspective of constructing materials with microstructures without thermodynamic or kinetics limitations. The underlying principles of selective deposition are briefly discussed below.

7.9.1 Area-Selective Growth

7.9.1.1 Epitaxial Growth Conditions

There is considerable technological interest today in area-selective epitaxy of both silicon and GaAs. A brief discussion of area-selective growth with reference to silicon and GaAs, respectively, is given below.

Epitaxial films can be grown at relatively high rates near equilibrium conditions, i.e. at a low driving force (low supersaturation) in the deposition process. For heterogeneous nucleation, a higher supersaturation is generally required. This means that conditions of selective growth prevail at supersaturations lower than that required for heterogeneous nucleation. This fact was used by Joyce and Baldrey for growth of silicon from SiCl_4 at 1200 °C and atmospheric

pressure in openings etched in a SiO_2 mask [63]. A historical review of selective epitaxial growth (SEG) was published by Borland [64]. In SEG, growth is stopped when the surface of the growing film reaches the mask surface. Continued growth results in an overgrowth over the mask. The process is then called epitaxial lateral overgrowth (ELO). For a review of the ELO process, the reader is referred to [65].

A key point in SEG is the suppression of nucleation on the mask (usually silicon oxide or silicon nitride). As mentioned in Section 7.7, the incubation time for nucleation varies with substrate material and deposition conditions. In an ideal case, the incubation time is longer than the deposition time required to prepare the desired structures. However, by using an alternating growth and etching process, SEG can be achieved even for conditions of short incubation times for nucleation [66]. Growth conditions then prevail for about the incubation time. After the growth cycle, the process is switched over to etching with, for example, HCl . A small amount of etching of single crystal silicon also occurs in the SiO_2 openings.

The GaAs SEG/ELO is nearly as old as the silicon SEG/ELO. Tausch and Lapierre reported in 1965 on a GaAs ELO process based on a chloride vapor transport system [67]. With the development of purification techniques for metal-organic compounds such as trimethyl gallium (TMG) and triethyl gallium (TEG), CVD as well as molecular beam epitaxy (MBE), based on the use of these compounds together with AsH_3 , are highly attractive for GaAs SEG. MBE and elemental sources yield single crystal growth in etched openings as well as polycrystalline GaAs on the mask (microstructure-selective deposition) [70]. GaAs SEG has received much attention during recent years as a technique for achieving monolithic integration of electronic and optoelectronic devices.

Growth of GaAs from AsH_3 and TMG by MBE or CVD is usually considered to be a non-equilibrium process. The perfection of the crystals grown, their morphology, and the correlation between growth rate and thermodynamic parameters indicates that near-equilibrium conditions exist at the interface between the vapor and the solid. Hence thermodynamics can be utilized to analyze selective growth as well heterogeneous nucleation conditions in GaAs CVD.

According to nucleation theory, a minimum supersaturation is needed for heterogeneous nucleation on the mask. From experimental selectivity data, the maximum supersaturation for maintaining selectivity can be calculated. The supersaturation is generally expressed in terms of chemical potentials. The influence of temperature on chemical potential of GaAs (expressed in elemental chemical potentials of Ga and As_2) at equilibrium with solid GaAs is shown in Figure 7.32. Growth will occur if the chemical potential of GaAs for homogeneous equilibrium in the vapor is higher than that for heterogeneous equilibrium.

The experimental technique used to determine the temperature required to achieve SEG is to raise the temperature successively until no nucleation on the mask can be observed. Since the

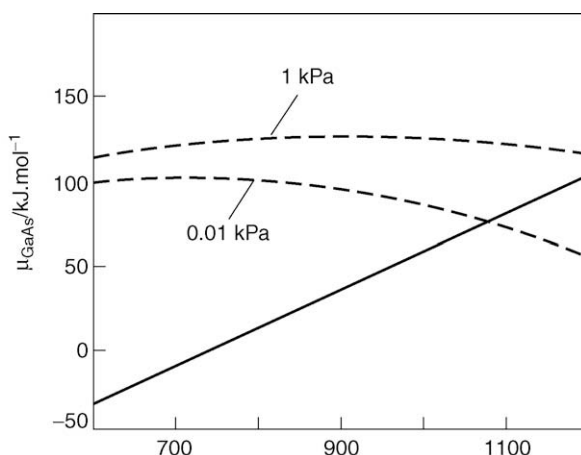


Figure 7.32: Chemical potential of GaAs for heterogeneous equilibrium (solid line), and for two homogeneous equilibria at different total pressures (dashed lines). $\text{H}_2/\text{AsH}_3/\text{TMG} = 500/10/1$ [68].

chemical potential of GaAs for the homogeneous equilibrium in the vapor has only a slight temperature dependence (Figure 7.2), the driving force for the deposition (or supersaturation) will decrease upon a temperature increase and a driving force value, yielding no heterogeneous nucleation, will be reached.

Thermodynamics and MBE and CVD experimental SEG data were used in an effort to put experimental selectivity observations on a common basis [69, 70]. A much lower pressure is used in MBE than in CVD. However, irrespective of the growth technique used, experimental SEG data fall in the supersaturation region indicated in Figure 7.33. By using thermodynamics, selectivity data from CVD can be converted to MBE and vice versa.

7.9.1.2 Substrate-Activated Selective Growth

When a substrate of a material other than that being deposited is exposed to the vapor in a CVD process, regions of different activities or reactivities are thus exposed. One material may, for example, act as an effective reducing agent or as a catalyst of dissociative adsorption of gaseous reactants, which may favor deposition. The other material may be relatively inert towards the vapor and growth will be inhibited. Inertness can be selectively increased by using gas additives which are preferentially adsorbed by one of the substrate materials. Strongly adsorbed molecules will strongly passivate a substrate surface and completely suppress the deposition process. A tendency toward substrate-activated area-selective growth is frequently seen during the initial growth stage in CVD on polycrystalline, multiphase substrates. Different phases and different crystallographic orientations of the grains exposed to the vapor represent surface regions of different activities/reactivities and initial growth conditions. Taken

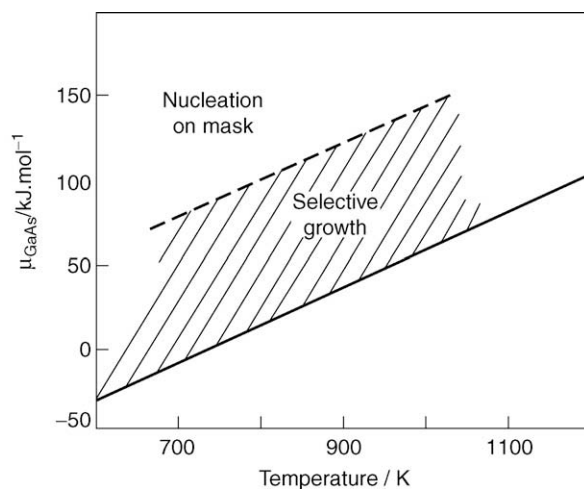
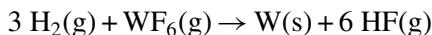


Figure 7.33: Selective growth regime for GaAs. Precursors: $\text{Ga}(\text{CH}_3)_3$, AsH_3 [70].

to its extreme, the end result is that deposition is inhibited on some substrate areas, while other areas are open for deposition.

Area-selective deposition of refractory metals is of highest interest for metallization in VLSI and ultra large scale integration (ULSI) processes. Selective deposition of refractory metals for metallization has been reviewed by several authors [71–74]. Substrate-activated area-selective growth is well illustrated by the selective tungsten deposition from WF_6 and H_2 on Si/SiO_2 substrates. This process is described below.

Tungsten can be deposited by CVD at low temperatures (300 °C) from H_2 and WF_6 according to the reaction



Deposition occurs on all substrate surfaces exposed to the vapor, since both the source material (WF_6) and reducing agent (H_2) are gases. However, if the reducing agent is replaced by a solid reducing agent (like elemental Si), deposition would occur only on those substrate regions having a reducing agent. Thus, tungsten is deposited only on the Si regions and not on adjacent SiO_2 regions. Si in SiO_2 cannot act as a reducing agent since this silicon has its maximum oxidation number. This is the basis of the initial stage of selective tungsten CVD.

Selective tungsten deposition may proceed according to the process described above as long as elemental Si is exposed to vapor. After a certain time, however, tungsten deposited onto elemental Si will separate Si from the vapor: hence a self-limiting growth process is obtained. The mechanism of self-limitation is still under discussion and may also be due to a polymerization reaction involving lower tungsten fluorides [75]. The polymer formed can also

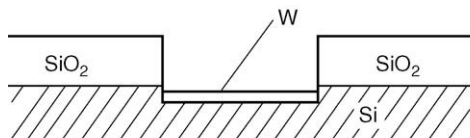
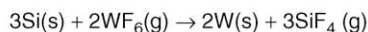
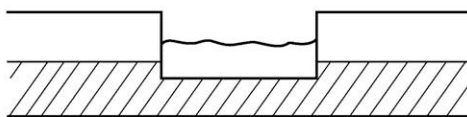
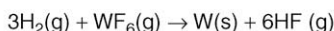
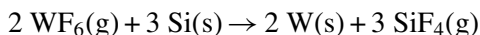
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Figure 7.34: The two reaction steps in selective tungsten CVD.

separate Si from the vapor, hence inhibiting the growth process. For growth of thicker tungsten layers, a reducing agent, H_2 , must be added to the reaction gas. If the WF_6 concentration is low and H_2 concentration is high enough, i.e. conditions for low supersaturation, tungsten will be deposited on previously deposited W (on elemental Si) and not on SiO_2 . For deposition onto SiO_2 , resulting in a loss of selectivity, tungsten nucleation must take place. This nucleation step requires a much higher supersaturation than growth. Hence there exists a deposition window, ranging from supersaturation corresponding to equilibrium conditions up to the value needed for heterogeneous tungsten nucleation on SiO_2 . Finally, selective deposition of tungsten to substrate regions where tungsten has already been deposited is favored by the dissociation of hydrogen molecules on these areas [76].

In summary, two main reaction steps can be distinguished in tungsten CVD (Figure 7.34):

1. Elemental Si will act as the predominant reducing agent even if a large amount of hydrogen is used in the reaction gas. This results in tungsten deposition on those substrate regions where elemental Si is exposed to the vapor. The reaction step includes an etching of elemental silicon, i.e. Si is consumed.



Considering the stoichiometry of this reaction, about 200 Å Si is consumed for 10 Å tungsten deposited. The topography of the Si/W interface is affected by this reaction. Etching and hence the topography can be reduced by, for example, addition of SiF_4 to the reaction gas mixture [77].

2. Another reducing agent, H_2 , must take over, since the tungsten film, and probably the resultant tungsten fluoropolymer, prevent reactions between the vapor and Si.

Chemical reactions in the first step are usually extremely fast and a thermodynamically controlled CVD process results. In the second process step, the deposition process is operated at low supersaturation to avoid nucleation on the mask material (SiO_2). Growth conditions in the second step are close to those existing in the area-selective epitaxy discussed above and can be described by thermodynamics. Thermodynamics is used as a guide for prediction of trends in selectivity and substrate etching when deposition conditions are changed. It has also been used for identification of plausible (and often undesired) side reactions as well as gaseous selectivity modifiers, improving selectivity [10].

7.9.1.3 Adsorption-Induced Selective Growth

As discussed above, heterogeneous nucleation on one of the substrate materials must be suppressed for a relatively long time in an ideal selective growth system. The incubation time for nucleation is influenced by many factors: temperature, substrate reactivity, adsorption, etc. Adsorbed molecules can reduce the rate of surface reactions and, in extreme, inhibit nucleation completely. The concept of strongly adsorbed molecules onto one of the substrate materials was used to achieve area-selective growth of boron carbide on a patterned substrate exposing areas of titanium (Ti) and molybdenum (Mo) to the vapor [78]. Boron trichloride, ethylene, and hydrogen were used as reactants and the deposition temperature was 1400 K. Ethylene molecules (or fragments of them) were preferentially and strongly adsorbed on molybdenum and no nucleation of boron carbide was observed. On titanium, however, fast nucleation kinetics was achieved. Deposition was located only on those substrate areas having titanium. Boron carbide was amorphous and contained about 21 at.% carbon. This illustrates that adsorbed molecules can act as masks and can be used to inhibit deposition on prescribed substrate regions.

7.9.2 Phase-Selective Deposition

A new dimension in the field of selective growth is realized in phase-selective growth. Phase-selective growth results when several phases are selectively and simultaneously deposited on prescribed substrate materials/regions. This can result in growth of, for example, a semiconductor together with an insulator, i.e. selectivity in properties is also achieved. Phase-selective deposition can be achieved in different ways. In this chapter, two principles of phase-selective growth are discussed: phase-selective deposition attained by differential nucleation behavior and by secondary processes in or on the growing film, respectively.

7.9.2.1 Phase-Selective Deposition by Differential Nucleation Behavior

Initial substrate/vapor reactions and nucleation kinetics are usually dependent on substrate material. This can result in nucleation of different phases on different substrate materials.

Provided that no secondary processes like phase transformation in the solid state occur in the film or that no new phase is nucleated on top of the growing film, the originally nucleated phases will continue to grow and a phase-selective deposition is obtained.

This principle is used for phase-selective growth of two boron carbides: Ti-BC_x and B_{13}C_2 . The substrate used is that obtained after area-selective growth of boron carbide described above, i.e. the substrate exposes molybdenum and amorphous boron carbide to the vapor. The vapor contained boron trichloride, methane, and hydrogen, and the growth temperature was 1400 K. Ti-BC_x was obtained on the amorphous boron carbide while B_{13}C_2 was grown on molybdenum. This phase-selective growth is attributed to differential nucleation kinetics since no secondary processes were observed in or on the films [79].

7.9.2.2 Phase-Selective Deposition Achieved Using Secondary Processes

Elemental boron (B) has several crystalline polymorphs and amorphous boron also exists. Phase-selective growth was studied in this system by using the Ti/Mo patterned substrates described above. Fast nucleation was observed on both Ti and Mo. Amorphous boron was obtained on Ti, while a-rhombohedral boron was grown on Mo. Boron grown on Ti contained a small amount of Ti (about 500 ppm) throughout the layers, while no traces of Mo was detected in a-B (detection limit 1 ppm). Titanium stabilizes the originally nucleated amorphous boron [80]. To obtain crystalline boron, a phase transformation in the solid state is needed and such a transformation can be assumed to have a high energy barrier to overcome. Amorphous boron can also be obtained initially on Mo. However, an immediate phase transformation is expected because of the deposition temperature used. Moreover, the film did not contain any substrate contaminants contributing to a stabilization of amorphous boron. The morphology of the phase-selectively deposited boron is shown in Figure 7.35. Amorphous boron is characterized by the rounded nodules.

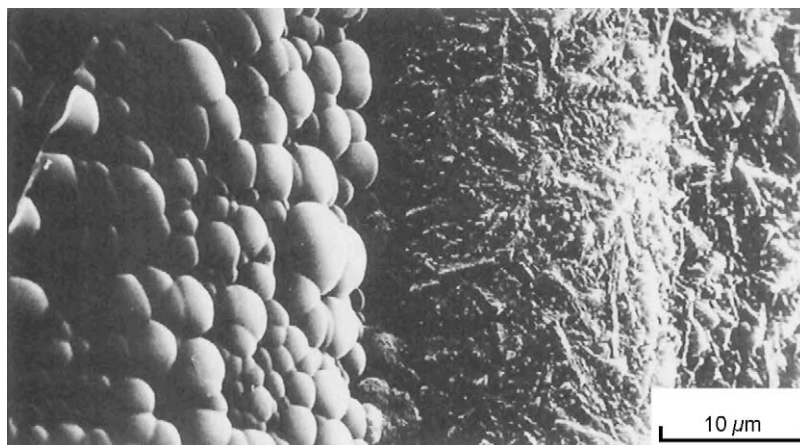


Figure 7.35: Phase-selective growth of amorphous boron (rounded nodules) and a-rhombohedral boron on a substrate exposing titanium and molybdenum [80].

7.10 Selected Applications of the CVD Technique

The CVD technique is known for its versatility in producing materials of greatly varying properties. This is illustrated by the examples given in the applications list below.

- *Microelectronics* industries use CVD for growth of epitaxial layers (vapor-phase epitaxy (VPE)) and for making films serving as dielectrics (low and high k), conductors, passivation layers, diffusion barriers, oxidation barriers, etc. An emerging field is selective deposition of refractory metals and silicides for metallization in VLSI.
- *Semiconductor lasers* of GaAs/(Ga,Al)As and InP/(In,Ga)As. These materials are also used in microwave devices and solar cells.
- *Optical fibers* for telecommunication. Optical fibers are produced by coating the inside of a fused silica tube with oxides of silicon, germanium, boron, etc., for obtaining the correct refractive index profile. After the deposition, a fused silica tube is collapsed to a rod and the rod is then drawn into a fiber.
- *Solar energy* conversion by the utilization of selective absorbers and of thin film solar cells of silicon and gallium arsenide, and dye sensitized solar cells.
- *Carbon nanotubes* for advance electronic, biological and chemical devices and detectors.
- *Wear-resistant* coatings have wide industrial applications. Coatings of TiC, TiN and Al_2O_3 on cemented carbide cutting-tool inserts and of TiC on steels (punches, nozzles, free wheels, etc.) are used extensively.
- *Friction-reducing* coatings for use in sliding and rolling contacts, for example.
- *Corrosion-resistant* coatings (Ta, Nb, Cr, etc.).
- *Erosion-resistant* coatings (TiC, Cr_7C_3 , B_4C , etc.).
- *Heat-resistant* coatings (Al_2O_3 , SiC, Si_3N_4 , etc.).
- *High temperature superconductors* for use in medical, power grid, high-energy physics applications. Examples are $\text{Bi}_2\text{Sr}_2\text{Ca}_n\text{Cu}_{n+1}\text{O}_{2n+6}$ (BSCCO) and $\text{YBa}_2\text{Cu}_3\text{O}_7$ (YBCO).
- *Fibers* for use in fiber-reinforced materials (fibers of boron, silicon carbide, boron carbide, etc.).
- *Structural shapes* (tubes, crucibles, heating elements, etc.) of, for example, tungsten and silicon carbide.
- *Decorative* coatings of, for example, TiN (gold color) on watches.
- *Conductive coatings* for integrated circuit interconnects, display applications, solar control, electrochromic windows, automotive windows.

7.11 Outlook

CVD offers many advantages in thin film deposition and has given birth to a wide variety of related technologies. With the use of new precursors and plasma enhancement deposition temperature can be lowered considerably. By lowering total pressure, extremely sharp interfaces with respect to chemical composition and topography can be obtained. Atmospheric pressure CVD is attractive for many applications with its high deposition rates and resulting short process times. Since CVD processes are based on interfacial chemistry, they are sensitive to contamination and loadlock systems must be used to keep the contamination level low. Selective deposition opens fascinating prospects for the future, not only for microelectronic applications but also for materials science in general, and for engineering of interfaces and artificial materials.

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