Chapter 5

Thin Film Growth

5.1 Molecular Beam Epitaxy[1]

NOTE: This module was developed as part of the Rice University course CHEM-496: *Chemistry of Electronic Materials*. This module was prepared with the assistance of Sarah Westcott.

5.1.1 Introduction

In the process of epitaxy, a thin layer of material is grown on a substrate. With respect to crystal growth it applies to the process of growing thin crystalline layers on a crystal substrate. In epitaxial growth, there is a precise crystal orientation of the film in relation to the substrate. For electronic devices, the substrate is a single crystal (usually Si or GaAs) and therefore so is the epitaxial layer (epilayer). In the most basic form of molecular beam epitaxy (MBE), the substrate is placed in ultra high vacuum (UHV) and the source materials for the film are evaporated from elemental sources. The evaporated molecules or atoms flow as a beam, striking the substrate, where they are adsorbed on the surface. Once on the surface, the atoms move by surface diffusion until they reach a thermodynamically favorable location to bond to the substrate. Molecules will dissociate to atomic form during diffusion or at a favorable site. Figure 5.1 illustrates the processes that can occur on the surface. Because the atoms require time for surface diffusion, the quality of the film will be better with slower growth. Typically growth rates of about 1 monolayer per second provide sufficiently high quality.

[1]This content is available online at <http://cnx.org/content/m25712/1.2/>.

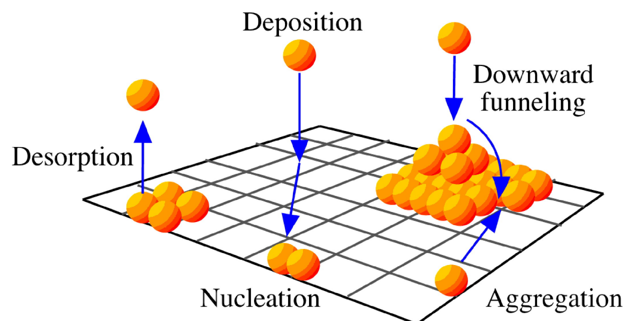

Figure 5.1: Schematic illustration of processes on growing surface during MBE. Adsorption of atoms on the surface, surface diffusion of atoms, formation of crystalline lattice, desorption of particles from the surface.

A typical MBE chamber is shown in Figure 5.2. The substrate is chemically washed and then put into a loading chamber where it is further cleaned using argon ion bombardment followed by annealing. This removes the top layers of the substrate, which is usually an undesired oxide which grew in air and contains impurities. The annealing heals any damage caused by the bombardment. The substrate then enters the growth chamber via the sample exchange load lock. It is secured on a molybdenum holder either mechanically or with melted indium or gallium which hold the substrate by surface tension.

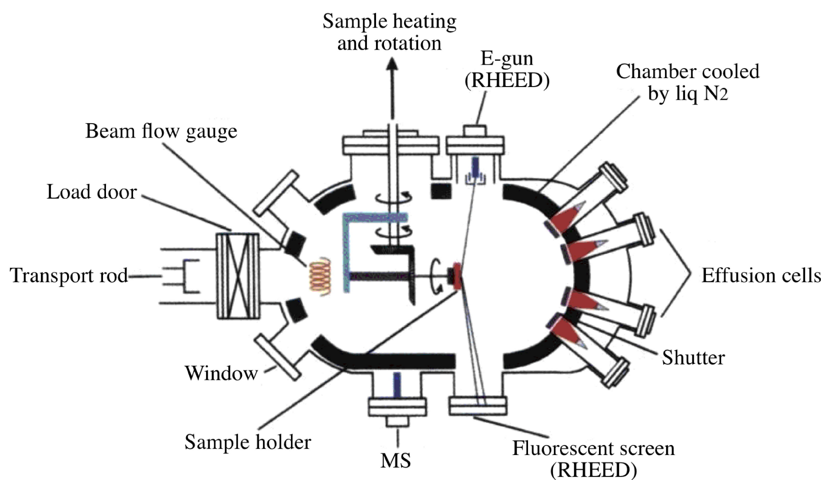

Figure 5.2: The MBE growth chamber.

Each effusion cell (see Figure 5.2) is a source of one element in the film. The effusion cell, also called a

Knudsen cell, contains the elemental form in very high purity (greater than 99.99999% for Ga and As). The cell is heated to encourage evaporation. For GaAs growth, the temperature is typically controlled for a vapor pressure of 10^{-2} to 10^{-3} Torr inside the effusion cell, which results in a transport of about 10^{15} molecules/cm^2 to the substrate when the shutter for that cell is opened. The shape and size of the opening in the cell is optimized for an even distribution of particles on the substrate. Due to the relatively low concentration of molecules, they typically do not interact with other molecules in the beam during the 5 - 30 cm journey to the substrate. The substrate is usually rotated, at a few rpm, to further even the distribution.

Because MBE takes place in UHV and has relatively low pressure of residual gas at the surface, analysis techniques such as reflection high energy diffraction and ellipsometry can be used during growth, both to study and control the growth process. The UHV environment also allows pre or post growth analysis techniques such as Auger spectroscopy.

5.1.2 Elemental and molecular sources

The effusion cell is used for the majority of MBE growth. All materials used in the cell are carefully chosen to be noninteracting with the element being evaporated. For example, the crucible is pyrolitic boron nitride. However, it has disadvantages, such as:

- The evaporated species may be molecular, rather than monomeric, which will require further dissocation at the surface.
- When the shutter is opened, the heat loss from the cell results in a transient in the beam flux which last for several minutes and cause variations of up to 50%.
- The growth chamber must be opened up to replace the solid sources.

Cracker cells are used to improve the ratio of monomeric to molecular (or at least dimeric to tetrameric) particles from the source. The cracker cell, placed so that the beam passes through it after the effusion cell, is maintained at a high temperature (and sometimes high pressure) to encourage dissociation. The dissociation process generally requires a catalyst and the best catalysts for a given species have been studied.

Some elements, such as silicon, have low enough vapor pressure that more direct heating techniques such as electron bombardment or laser radiation heating are used. The electron beam is bent using electromagnetic focusing to prevent any impurities in the electron source from contaminating the silicon to be used in MBE. Because the heat is concentrated on the surface to be evaporated, interactions with and contamination from the crucible walls is reduced. In addition, this design does not require a shutter, so there is no problem with transients. Modulation of the beam can produce very sharp interfaces on the substrate. In laser radiation heating, the electron beam is replaced by a laser beam. The advantages of localized heating and rapid modulation are also maintained without having to worry about contamination from the electron source or stray electrons.

Some of the II-VI (12-16) compounds have such high vapor pressure that a Knudson cell cannot be used. For example, the mercury source must be kept cooler than the substrate to keep the vapor pressure low enough to be feasible. The Hg source must also be sealed off from the growth chamber to allow the chamber to be pumped down.

Two other methods of obtaining the elements for use in epitaxy are gas-source epitaxy and chemical beam epitaxy (CBE). Both of these methods use gas sources, but they are distinguished by the use of elemental beams in gas source epitaxy, while organometallic beams are used in CBE. For the example of III-V (13-15) semiconductors, in gas epitaxy, the group III material may come from an effusion cell while the group V material is the hydride, such as AsH_3 or PH_3, which is cracked before entering the growth chamber. In CBE, the group V material is an organometallic, such as triethylgallium $[Ga(C_2H_5)_3]$ or trimethylaluminum $[Al(CH_3)_3]$, which adsorbs on the surface, where it dissociates.

The gas sources have several advantages. Gas lines can be run into the chamber, which allows the supply to be replenished without opening the chamber. When making alloys, such as $Al_xGa_{1-x}As$, the gases can be premixed for the correct stochiometry or even have their composition gradually changed for making graded structures. For abrupt structures, it is necessary to be able to switch the gas lines with speeds of 1 second or less. However, the gas lines increase the complexity of the process and can be hard on the pumping system.

5.1.3 Substrate choice and preparation

Materials can be grown on substrates of different structure, orientation, and chemistry. In deciding which materials can be grown on a particular substrate, a primary consideration was expected to be lattice mismatch, i.e., differences in spacing between atoms. However, while lattice mismatch can cause strain in the grown layer, considerable accommodation between materials of different sizes can take place during growth. A greater source of strain can be differences in thermal expansion characteristics because the layer is grown at high temperature. On cooling to room temperature, dislocation defects can be formed at the interface or in severe cases, the device may break. Chemical considerations, such as whether the layer's elements will dissolve in the substrate or form compounds with the substrate, must also be considered.

Different orientations of the substrate can also affect growth. Close-packed planes have the lowest surface energy, which allows atoms to desorb from the surface, resulting in slower growth rates. Growth is favored where bonds can be made in several directions at the same time. Therefore, the substrate is often cut off-axis by a 2 - 4 ° to provide a rougher growth surface. For compound semiconductors, some orientations result in the number of loose bonds changing between layers. This results in changes of surface energy with each layer, which slows growth down.

The greatest cause of defects in the epitaxial layer is defects on the substrate's surface. In general, any dislocations on the substrate are replicated or even multiplied in the epitaxial growth, which is what makes the cleaning of the substrate so important.

5.1.4 Materials grown

MBE is commercially used primarily for GaAs devices. This is partly because the high speed microwave devices made from GaAs required the superior electrical quality of epitaxial layers. Taking place at lower temperature and under better controlled conditions, MBE generally results in layers of better quality than melt-grown.

From solid Ga and As sources, elemental Ga and tetrameric As_4 are evaporated. For a GaAs substrate, the Ga flux has a sticking coefficient very close to 1 (almost certain to adsorb). The As is much less likely to adsorb, so an excess is usually supplied. Cracker cells are often used on the As_4 in order to obtain As_2 instead, which results in faster growth and more efficient utilization of the source beam.

For nominally undoped GaAs grown by MBE, the residual impurities are usually carbon, from substrate contamination and residual gas after the growth chamber is pumped down, and sulphur, from the As source. The most common surface defects are "oval" defects, which seem to form when Ga manages to form metallic droplets during the growth process, which can particularly occur if the substrate was not cleaned properly. These defects can also be reduced by carefully controlling the Ga flux.

During MBE growth, dopants can be introduced by having a separate effusion cell or gas source for each dopant. To achieve a desired dopant concentration in the film, not only must the rate of dopants striking the substrate be controlled, but the characteristics of how the dopant behaves on the surface must be known. Low-vapor pressure dopants tend to desorb from the surface and their behavior is very temperature dependent and so are avoided when possible. Slow diffusing dopants adsorb to surface sites and are eventually covered as more GaAs is grown. Their incorporation depends linearly on the partial pressure of the dopant present in the growth chamber. This is the behavior exhibited by most n-type dopants in GaAs and most dopants of both types in Si. If the dopant, like most p-type GaAs dopants, is able to diffuse through the surface of the substrate into the crystal below, then there will be higher incorporation efficiency, which will depend on the square root of the dopant partial pressure for reasonable concentrations. Due to increasing lattice strain, all dopants will saturate at very high concentrations. They may also tend to form clusters. Dopant behavior depends on many factors and is actively studied.

The growth of GaAs epitaxial layers on silicon substrates has also been investigated. Silicon substrates are grown in larger wafers, have better thermal conductivity allowing more devices/chip to be grown on them, and are cheaper. However, because Si is nonpolar and GaAs is polar, the GaAs tends to form islands on the surface with different phase (what should be a Ga site based on a neighboring domain's pattern will actually be an As site). There is also a fairly large lattice mismatch, leading to may dislocations. However,

FETs, LEDs, and lasers have all been made in laboratories.

Many devices require abrupt junctions between layers of different materials. One group, studying how to make high quality, abrupt GaAs and AlAs layers, found that rapid movement of the Ga or Al on the surface was required. This migration was enhanced at high temperatures, but unfortunately, diffusion into the substrate also increased. However, they also discovered that migration of Ga or Al increased if the As supply was turned off. By alternating the Ga and As supplies, the Ga was able to reach the substrate and migrate to provide more even monolayer coverage before the As atoms arrived to react.

Besides GaAs, most other III-V semiconductors have also been grown using MBE. Structures involving very thin layers (only a few atomic layers thick), often called superlattices or strained superlattices if there is a large lattice mismatch, are routinely grown. Because different materials have different energy levels for electrons and holes, it is possible to trap carriers in one of these thin layers, forming a quantum well. This type of confinement structure is particularly popular for LEDs or lasers, including blue light lasers. The strained superlattice structure actually shifts and splits the energy levels of the materials in some cases making devices possible for such applications as infrared light detection, which requires very small band gaps.

Thin films of many other materials have also been grown using MBE methods. Silicon technology has cheaper methods of growth and so Si layers are not very popular. However, possible devices made of Si-Ge alloys have been grown. The II-VI compounds, have also been grown. Magnetic materials, such as Co-Pt and Fe-Pt alloys, have been grown in the hopes of providing better magnetic storage.

5.1.5 Analysis techniques

The most popular in-situ analysis technique for MBE-grown layers is reflection high energy diffraction (RHEED), see Figure 5.3. Electrons of energy 5 - 40 keV are directed towards the sample. They reflect from the surface at a very small angle (less than 3 °) and are directed onto a screen. These electrons interact with only the top few atomic layers and thus provide information about the surface. Figure 5.4 shows a typical pattern on the screen for electrons reflected from a smooth surface, in which constructive interference between some of the electrons reflected from the lattice structure results in lines. If the surface is rough, spots will appear on the screen, also. By looking at the total intensity of the reflected electron pattern, an idea of the number of monolayers deposited and how epilayers grow can be obtained. The island-type growth shown in this figure is an area of intense interest. These oscillations in intensity are gradually damped as more layers are grown, because the overall roughness of the surface increases.

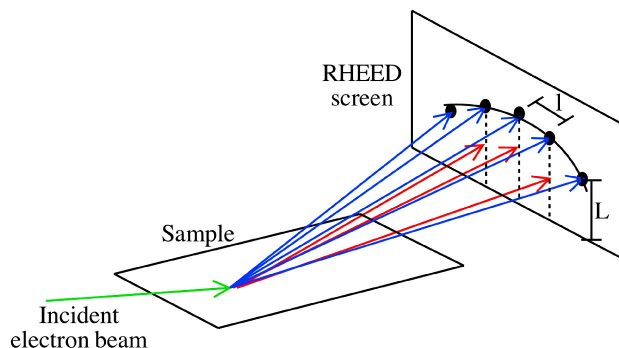

Figure 5.3: Schematic illustrating the formation of a RHEED pattern.

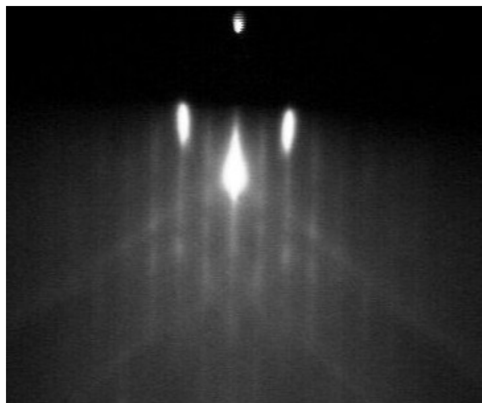

Figure 5.4: RHEED diffraction pattern of a GaAs surface. Adapted from images by the MBE Laboratory in the Institute of Physics of the ASCR (http://www.fzu.cz/departments/surfaces/mbe/index.html).

Phase locked epitaxy takes advantage of the patterns of the oscillations to grow very abrupt layers. By sending the oscillation information to a computer, it can decide when to open or close the shutters of the effusion cell based on the location in the oscillation cycle. This technique self-adjusts for fluctuations in beam flux when the shutters are opened and can grow very abrupt layers.

Another analysis technique that can be used to study surface smoothness during growth is ellipsometry. Polarized laser light is reflected from the surface at a small angle. The polarization of the light changes, depending on the roughness of the surface.

Improved growth characteristics also require that the actual flux from the sources is measured. This is typically done with an ion gauge flux monitor, which is either used to measure residual beam that misses the substrate or is moved into the beam path for calibration when a new source is used. Because of the importance of clean substrate surfaces for low-defect growth, Auger spectroscopy is used following cleaning by sputtering. Auger spectroscopy takes place by ionizing an inner shell electron from an atom. When an outer shell electron then deexcites to the inner shell, the energy released can prompt the emission of another outer shell electron. The energy at which this occurs is characteristic of the atom involved and the signal can be used to detect impurities as small as 0.1%.

5.1.6 Bibliography

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5.2 Atomic Layer Deposition[2]

This module was developed as part of the Rice University course CHEM-496: *Chemistry of Electronic Materials*. This module was prepared with the assistance of Julie A. Francis.

5.2.1 Introduction

The growth of thin films has had dramatic impact on technological progress. Because of the various properties and functions of these films, their applications are limitless especially in microelectronics. These layers can act as superconductors, semiconductors, conductors, insulators, dielectric, or ferroelectrics. In semiconductor devices, these layers can act as active layers and dielectric, conducting, or ion barrier layers. Depending on the type of film material and its applications, various deposition techniques may be employed. For gas-phase deposition, these include vacuum evaporation, reactive sputtering, chemical vapor deposition (CVD), especially metal organic CVD (MOCVD), and molecular beam epitaxy (MBE). Atomic layer deposition (ALD), originally called atomic layer epitaxy (ALE), was first reported by Suntola et al. in 1980 for the growth of zinc sulfide thin films to fabricate electroluminescent flat panel displays.

ALD refers to the method whereby film growth occurs by exposing the substrate to its starting materials alternately. It should be noted that ALE is actually a sub-set of ALD, in which the grown film is epitaxial to the substrate; however, the terms are often used interchangeably. Although both ALD and CVD use chemical (molecular) precursors, the difference between the techniques is that the former uses self limiting chemical reactions to control in a very accurate way the thickness and composition of the film deposited. In this regard ALD can be considered as taking the best of CVD (the use of molecular precursors and atmospheric or low pressure) and MBE (atom-by-atom growth and a high control over film thickness) and combining them in single method. A selection of materials deposited by ALD is given in Table 5.1.

Compound class	**Examples**
II–VI compounds	ZnS, ZnSe, ZnTe, $ZnS_{1-x}Se_x$, CaS, SrS, BaS, $SrS_{1-x}Se_x$, CdS, CdTe, MnTe, HgTe, $Hg_{1-x}Cd_xTe$, $Cd_{1-x}Mn_xTe$
II–VI based thin-film electroluminescent (TFEL) phosphors	ZnS:M (M = Mn, Tb, Tm), CaS:M (M = Eu, Ce, Tb, Pb), SrS:M (M = Ce, Tb, Pb, Mn, Cu)
III–V compounds	GaAs, AlAs, AlP, InP, GaP, InAs, $Al_xGa_{1-x}As$, $Ga_xIn_{1-x}As$, $Ga_xIn_{1-x}P$
Semiconductors/dielectric nitrides	AlN, GaN, InN, SiN_x
Metallic nitrides	TiN, TaN, Ta_3N_5, NbN, MoN
Dielectric oxides	Al_2O_3, TiO_2, ZrO_2, HfO_2, Ta_2O_5, Nb_2O_5, Y_2O_3, MgO, CeO_2, SiO_2, La_2O_3, $SrTiO_3$, $BaTiO_3$
Transparent conductor oxides	In_2O_3, In_2O_3:Sn, In_2O_3:F, In_2O_3:Zr, SnO_2, SnO_2:Sb, ZnO,

continued on next page

[2]This content is available online at <http://cnx.org/content/m25737/1.2/>.

Semiconductor oxides	ZnO:Al, Ga_2O_3, NiO, CoO_x
Superconductor oxides	$YBa_2Cu_3O_{7-x}$
Fluorides	CaF_2, SrF_2, ZnF_2

Table 5.1: Examples of thin film materials deposited by ALD including films deposited in epitaxial, polycrystalline or amorphous form. Adapted from M. Ritala and M. Leskel, *Nanotechnology*, 1999, **10**, 19.

5.2.2 How ALD works

The premise behind the ALD process is a simple one. The substrate (amorphous or crystalline) is exposed to the first gaseous precursor molecule (elemental vapor or volatile compound of the element) in excess and the temperature and gas flow is adjusted so that only one monolayer of the reactant is chemisorbed onto the surface (Figure 5.5a). The excess of the reactant, which is in the gas phase or physisorbed on the surface, is then purged out of the chamber with an inert gas pulse before exposing the substrate to the other reactant (Figure 5.5b). The second reactant then chemisorbs and undergoes an exchange reaction with the first reactant on the substrate surface (Figure 5.5c). This results in the formation of a solid molecular film and a gaseous side product that may then be removed with an inert gas pulse (Figure 5.5d).

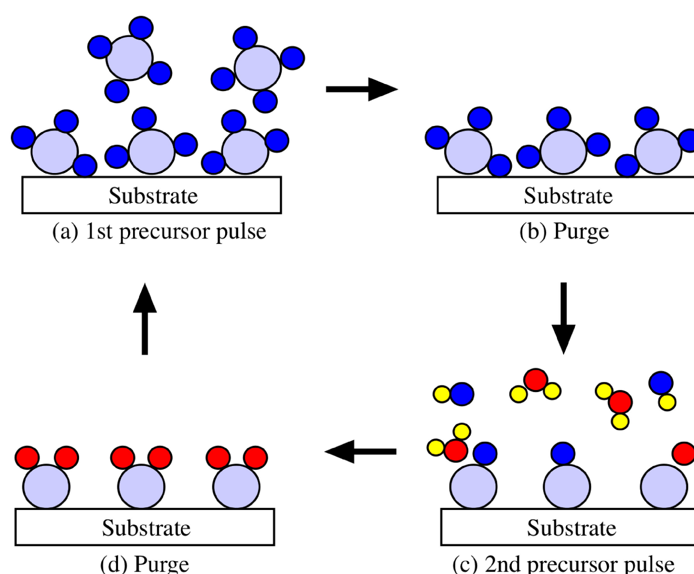

Figure 5.5: Schematic representation of an ALD process.

The deposition may be defined as self-limiting since one, and only one, monolayer of the reactant species remains on the surface after each exposure. In this case, one complete cycle results in the deposition of one monolayer of the compound on the substrate. Repeating this cycle leads to a controlled layer-by-layer growth. Thus the film thickness is controlled by the number of precursor cycles rather than the deposition time, as is the case for a CVD processes. This self-limiting behavior is the fundamental aspect of ALD and understanding the underlying mechanism is necessary for the future exploitation of ALD.

One basic condition for a successful ALD process is that the binding energy of a monolayer chemisorbed on a surface is higher than the binding energy of subsequent layers on top of the formed layer; the temperature of the reaction controls this. The temperature must be kept low enough to keep the monolayer on the surface until the reaction with the second reactant occurs, but high enough to re-evaporate or break the chemisorption bond. The control of a monolayer can further be influenced with the input of extra energy such as UV irradiation or laser beams. The greater the difference between the bond energy of a monolayer and the bond energies of the subsequent layers, the better the self-controlling characteristics of the process.

Basically, the ALD technique depends on the difference between chemisorption and physisorption. Physisorption involves the weak van der Waal's forces, whereas chemisorption involves the formation of relatively strong chemical bonds and requires some activation energy, therefore it may be slow and not always reversible. Above certain temperatures chemisorption dominates and it is at this temperature ALD operates best. Also, chemisorption is the reason that the process is self-controlling and insensitive to pressure and substrate changes because only one atomic or molecular layer can adsorb at the same time.

5.2.3 Equipment for the ALD process

Equipment used in the ALD process may be classified in terms of their working pressure (vacuum, low pressure, atmospheric pressure), method of pulsing the precursors (moving substrate or valve sources) or according to the types of sources. Several system types are discussed.

In a typical moving substrate ALD growth system (Figure 5.6) the substrate, located in the recess part of the susceptor, is continuously rotated and cuts through streams of the gaseous precursors, in this case, trimethylgallium [TMG, $Ga(CH_3)_3$] and arsine (AsH_3). These gaseous precursors are introduced through separate lines and the gases come in contact with the substrate only when it revolves under the inlet tube. This cycle is repeated until the required thickness of GaAs is achieved. The exposure time to each of the gas streams is about 0.3 s.

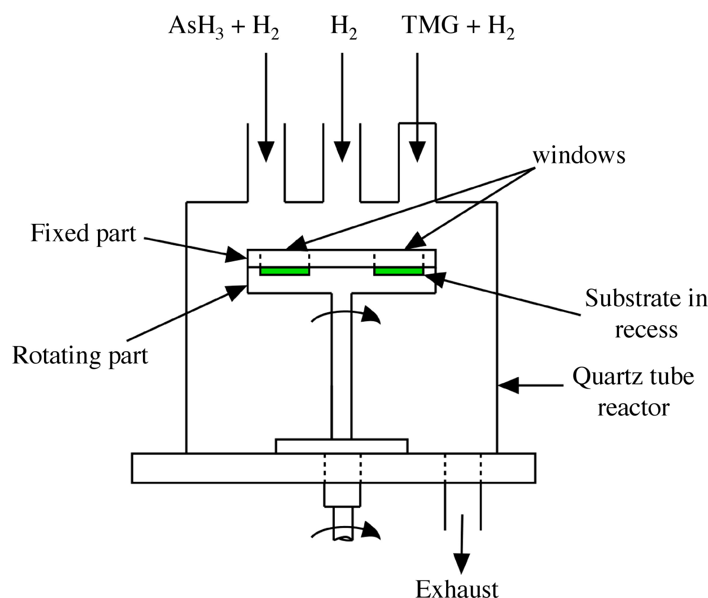

Figure 5.6: A typical moving substrate ALD growth system used to grow GaAs films. Adapted from M. A. Tischler and S. M. Bedair, *Appl. Phys. Lett.*, 1986, **48**, 1681.

ALD may be carried out in a vacuum system using an ultra-high vacuum with a movable substrate holder and gaseous valving. In this manner it may be also equipped with an in-situ LEED system for the direct observation of surface atom configurations and other systems such as XPS, UPS, and AES for surface analysis.

A lateral flow system may also be employed for successful ALE deposition. This uses an inert gas flow for several functions; it transports the reactants, it prevents pump oil from entering the reaction zone, it valves the sources and it purges the deposition site between pulses. Inert gas valving has many advantages as it can be used at ultra high temperatures where mechanical valves may fail and it does not corrode as mechanical valves would in the presence of halides. This method is based on the fact that as the inert gas is flowing through the feeding tube from the source to the reaction chamber, it blocks the flow of the sources. Although in this system the front end of the substrate receives a higher flux density than the down-stream end, a uniform growth rate occurs as long as the saturation layer of the monoformation predominates. This lateral flow system effectively utilizes the saturation mechanism of a monolayer formation obtained in ALE. Depending on the properties of the precursors used, and on the growth temperature, various growth systems may be used for ALE.

5.2.4 Requirements for ALD growth

Several parameters must be taken into account in order to assure successful ALD growth. These include the physical and chemical properties of the source materials, their pulsing into the reactor, their interaction with the substrate and each other, and the thermodynamics and volatility of the film itself.

Source molecules used in ALD can be either elemental or an inorganic, organic, or organometallic compound. The chemical nature of the precursor is insignificant as long as it possesses the following properties.

It must be a gas or must volatilize at a reasonable temperature producing sufficient vapor pressure. The vapor pressure must be high enough to fill the substrate area so that the monolayer chemisorption can occur in a reasonable length of time. Note that prolonged exposure to the substrate can cause the precursor to condense on the surface hindering the growth. Chemical interaction between the two precursors prior to chemisorption on the surface is also undesired. This may be overcome by purging the surface with an inert gas or hydrogen between the pulses. The inert gas not only separates the reactant pulses but also cleans out the reaction area by removing excess molecules. Also, the source molecules should not decompose on the substrate instead of chemisorbing. The decomposition of the precursor leads to uncontrolled growth of the film and this defeats the purpose of ALD as it no longer is self-controlled, layer-by-layer growth and the quality of the film plummets.

In general, temperature remains the most important parameter in the ALD process. There exists a processing window for ideal growth of monolayers. The temperature behavior of the rate of growth in monolayer units per cycle gives a first indication of the limiting mechanisms of an ALD process. If the temperature falls too low, the reactant may condense or the energy of activation required for the surface reaction may not be attained. If the temperature is too high, then the precursor may decompose or the monolayer may evaporate resulting in poor ALD growth. In the appropriate temperature window, full monolayer saturation occurs meaning that all bonding sites are occupied and a growth rate of one lattice unit per cycle is observed. If the saturation density is below one, several factors may contribute to this. These include an oversized reactant molecule, surface reconstruction, or the bond strength of an adsorbed surface atom is higher when the neighboring sites are unoccupied. Then the lower saturation density may be thermodynamically favored. If the saturation density is above one, then the undecomposed precursor molecules form the monolayer. Generally, ideal growth occurs when the temperature is set where the saturation density is one.

5.2.5 Advantages of ALD

Atomic layer deposition provides an easy way to produce uniform, crystalline, high quality thin films. It has primarily been directed towards epitaxial growth of III-V (13-15) and II-V (12-16) compounds, especially to layered structures such as superlattices and superalloys. This application is due to the greatest advantage of this method, it is controllable to an accuracy of a single atomic layer because of saturated surface reactions. Not only that, but it produces epitaxial layers that are uniform over large areas, even on non-planar surfaces, at temperatures lower than those used in conventional epitaxial growth.

Another advantage to this method that may be most important for future applications, is the versatility associated with the process. It is possible to grow different thin films by choosing suitable starting materials among the thousands of available chemical compounds. Provided that the thermodynamics are favorable, the adjustment of the reaction conditions is a relatively easy task because the process is insensitive to small changes in temperature and pressure due to its relatively large processing window. There are also no limits in principle to the size and shape of the substrates.

One advantage that is resultant from the self-limiting growth mechanism is that the final thickness of the film is dependent only upon the number of deposition cycles and the lattice constant of the material, and can be reproduced and controlled. The thickness is independent of the partial pressures of the precursors and growth temperature. Under ideal conditions, the uniformity and the reproducibility of the films are excellent. ALE also has the potential to grow very abrupt heterostructures and very thin layers and these properties are in demand for some applications such as superlattices and quantum wells.

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5.3 Chemical Vapor Deposition[3]

NOTE: This module was developed as part of the Rice University course CHEM-496: *Chemistry of Electronic Materials*. This module was prepared with the assistance of Scott Stokes.

5.3.1 Introduction

Chemical vapor deposition (CVD) is a deposition process where chemical precursors are transported in the vapor phase to decompose on a heated substrate to form a film. The films may be epitaxial, polycrystalline or amorphous depending on the materials and reactor conditions. CVD has become the major method of film deposition for the semiconductor industry due to its high throughput, high purity, and low cost of operation. CVD is also commonly used in optoelectronics applications, optical coatings, and coatings of wear resistant parts.

CVD has many advantages over physical vapor deposition (PVD) processes such as molecular beam evaporation and sputtering. Firstly, the pressures used in CVD allow coating of three dimensional structures with large aspect ratios. Since evaporation processes are very directional, PVD processes are typically line of sight depositions that may not give complete coverage due to shadowing from tall structures. Secondly, high precursor flow rates in CVD give deposition rates several times higher than PVD. Also, the CVD reactor is relatively simple and can be scaled to fit several substrates. Ultra-high vacuum is not needed for CVD and changes or additions of precursors is an easy task. Furthermore, varying evaporation rates make stoichiometry hard to control in physical deposition. While for CVD stoichiometry is more easily controlled by monitoring flow rates of precursors. Other advantages of CVD include growth of high purity films and the ability to fabricate abrupt junctions.

There are, however, some disadvantages of CVD that make PVD more attractive for some applications. High deposition temperatures for some CVD processes (often greater than 600 °C) are often unsuitable for structures already fabricated on substrates. Although with some materials, use of plasma-enhanced CVD or metal-organic precursors may reduce deposition temperatures. Another disadvantage is that CVD precursors are often hazardous or toxic and the by-products of these precursors may also be toxic. Therefore extra steps have to be taken in the handling of the precursors and in the treatment of the reactor exhaust. Also, many precursors for CVD, especially the metal-organics, are relatively expensive. Finally, the CVD process contains a large number of parameters that must be accurately and reproducibly optimized to produce good films.

5.3.2 Kinetics of CVD

A normal CVD process involves complex flow dynamics since gases are flowing into the reactor, reacting, and then by-products are exhausted out of the reactor. The sequence of events during a CVD reaction are shown in Figure 5.7 and as follows:

1) Precursor gases input into the chamber by pressurized gas lines.
2) Mass transport of precursors from the main flow region to the substrate through the boundary layer (Figure 5.7a);
3) Adsorption of precursors on the substrate (normally heated) (Figure 5.7b).
4) Chemical reaction on the surface (Figure 5.7c)
5) Atoms diffuse on the surface to growth sites.
6) Desorption of by-products of the reactions (Figure 5.7d).
7) Mass transport of by-products to the main flow region (Figure 5.7e).

[3]This content is available online at <http://cnx.org/content/m25495/1.2/>.

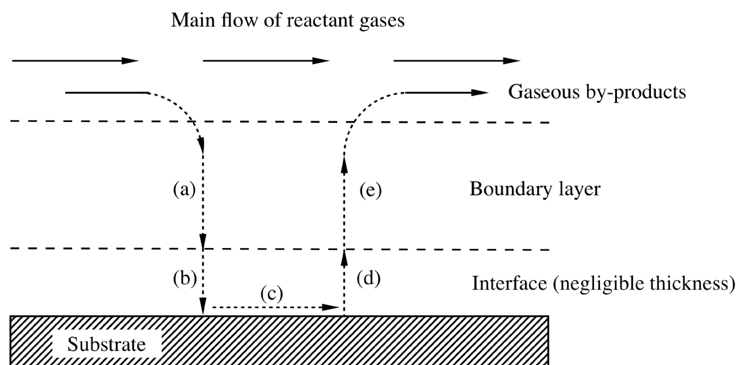

Figure 5.7: Sequence of events during CVD: (a) diffusion of reactants through boundary layer, (b) adsorption of reactants on substrate, (c) chemical reaction takes place, (d) desorption of adsorbed species, and (e) diffusion out of by-products through boundary layer. Adapted from H. O. Pierson, *Handbook of Chemical Vapor Deposition*, Noyes Publications, Park Ridge (1992).

5.3.2.1 The boundary layer

Gas flow in a CVD reactor is generally laminar, although in some cases heating of the chamber walls will create convection currents. The complete problem of gas flow through the system is too complex to be described here; however, assuming we have laminar flow (often a safe assumption) the gas velocity at the chamber walls will be zero. Between the wall (zero velocity) and the bulk gas velocity there is a boundary layer. The boundary layer thickness increases with lowered gas velocity and the distance from the tube inlet (Figure 5.8). Reactant gases flowing in the bulk must diffuse through the boundary layer to reach the substrate surface. Often, the susceptor is tilted to partially compensate for the increasing boundary-layer thickness and concentration profile.

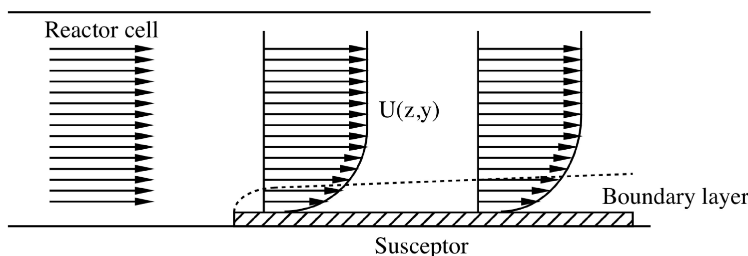

Figure 5.8: Development of boundary layer in a horizontal reactor. Adapted from G. B. Stringfellow, *Organometallic Vapor-Phase Epitaxy: Theory and Practice*, Academic Press, New York (1994).

5.3.2.2 Rate limiting steps

During CVD the growth rate of the film is limited by either surface reaction kinetics, mass transport (diffusion) of precursors to the substrate, or the feed rate of the precursors.

Surface reaction controls the rate when growth occurs at low temperatures (where the reaction occurs slowly) and also dominates at low pressures (where the boundary layer is thin and reactants easily diffuse to the surface), see Figure 5.9. Since reactants easily diffuse through the boundary layer, the amount of reactant at the surface is independent of reactor pressure. Therefore, it is the reactions and motions of the precursors adsorbed on the surface which will determine the overall growth rate of the film. A sign of surface reaction limited growth would be dependence of the growth rate on substrate orientation, since the orientation would certainly not affect the thermodynamics or mass transport of the system.

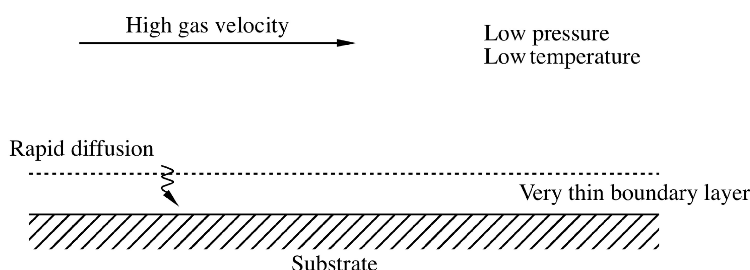

Figure 5.9: Surface reaction limited growth in CVD. Adapted from H. O. Pierson, *Handbook of Chemical Vapor Deposition*, Noyes Publications, Park Ridge (1992).

A deposition limited by mass transport is controlled by the diffusion of reactants through the boundary layer and diffusion of by-products out of the boundary layer. Mass transport limits reactions when the temperature and pressure are high. These conditions increases the thickness of the boundary layer and make it harder for gases to diffuse through (Figure 5.10). In addition, decomposition of the reactants is typically quicker since the substrate is at a higher temperature. When mass transport limits the growth, either increasing the gas velocity or rotating the substrate during growth will decrease the boundary layer and increase the growth rate.

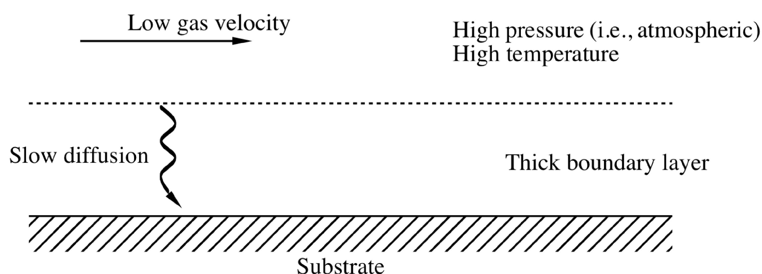

Figure 5.10: Mass transport limited growth in CVD. Adapted from H. O. Pierson, *Handbook of Chemical Vapor Deposition*, Noyes Publications, Park Ridge (1992).

Feed rate limits the deposition when nearly all the reactant is consumed in the chamber. The feed rate is more important for a hot wall reactor since the heated walls will decompose a large amount of the precursor. Cold wall reactors tend to have higher deposition rates since the reactants are not depleted by the walls.

A plot of growth rate versus temperature, known as an Arrhenius plot, can be used to determine the rate limiting step of a reaction (Figure 5.11). Mass transport limits reactions at high temperatures such that growth rate increases with partial pressures of reactants, but is constant with temperature. Surface reaction kinetics dominates at low temperatures where the growth rate increases with temperature, but is constant with pressures of reactants. Feed rate limited reactions are independent of temperature, since it is the rate of gas delivery that is limiting the reaction. The Arrhenius plot will show where the transition between the mass transport limited and the surface kinetics limited growth occurs in the temperature regime.

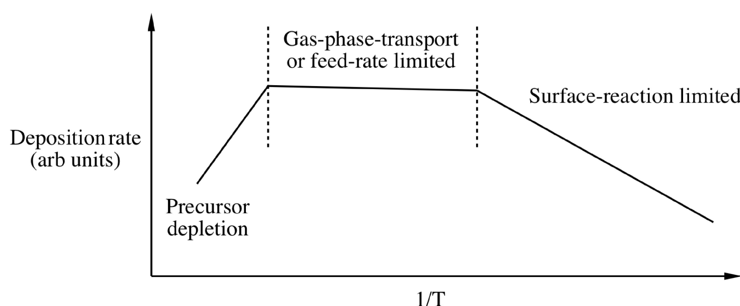

Figure 5.11: Dependence of CVD deposition rate on temperature. Adapted from J. G. Eden, in *Thin Film Processes II*, Eds. J. L. Vossen and W. Kern, Academic Press, New York (1991).

Increases in reactant concentrations will to a point increase the deposition rate. However, at very high reactant concentrations, gas phase nucleation will occur and the growth rate will drop (Figure 5.12). Slow deposition in a CVD reactor can often be attributed to either gas phase nucleation, precursor depletion due to hot walls, thick boundary layer formation, low temperature, or low precursor vapor pressure.

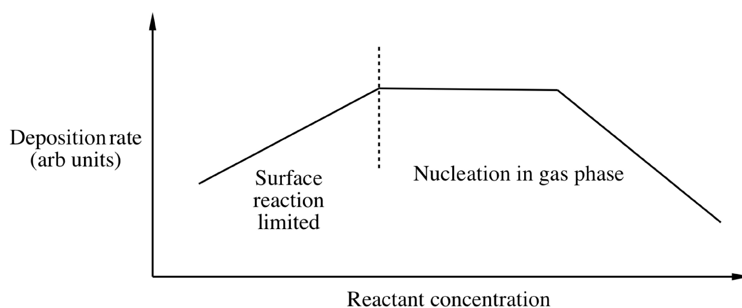

Figure 5.12: Demonstration of deposition rate on reactant concentration for CVD deposition. Adapted from J. G. Eden, in *Thin Film Processes II*, Eds. J. L. Vossen and W. Kern, Academic Press, New York (1991).

5.3.3 CVD systems

5.3.3.1 Precursor delivery

Flow of reactants into the reactor must be closely monitored to control stoichiometry and growth rate. Precursor delivery is very important since in many cases the flow rate can limit the deposition. For low vapor pressure solids, a carrier gas is passed over or through a bed of the heated solid to transport the vapor into the reactor. Gas flow lines are usually heated to reduce condensation of the vapor in the flow lines. In the case of gas precursors, mass flowmeters easily gauge and control the flow rates. Liquid precursors are normally heated in a bubbler to achieve a desired vapor pressure (Figure 5.13).

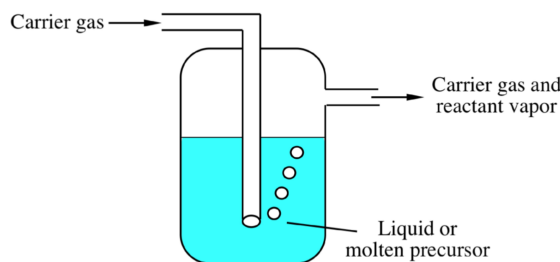

Figure 5.13: Schematic representation of a bubbler for liquid precursors.

An inert gas such as hydrogen is bubbled through the liquid and by calculating the vapor pressure of the reactant and monitoring the flow rate of the hydrogen, the flow rate of the precursor is controlled by using (5.1), where Q_{MO} is the flow rate of the metal-organic precursor, Q_{H2} is the flow rate of hydrogen through the bubbler, P_{MO} is the vapor pressure of the metal-organic at the bubbler temperature, and P_B is

the pressure of the bubbler.

$$Q_{MO} = Q_{H2} \times \frac{P_{MO}}{P_B - P_{MO}} \tag{5.1}$$

Another method of introducing liquid precursors involves flash vaporization where the liquid is passed into a flask heated above the boiling point of the liquid. The gas vapor is then passed through heated lines to the CVD chamber. Often, a carrier gas is added to provide a fixed flow rate into the reactor. This method of precursor introduction is useful when the precursor will decompose if heated over time. A similar technique called spray pyrolysis introduces the precursors in the form of aerosol droplets. The droplets evaporate in the chamber from the heated gas above the substrate or heated chamber walls (Figure 5.14). Then the reaction proceeds as a normal CVD process.

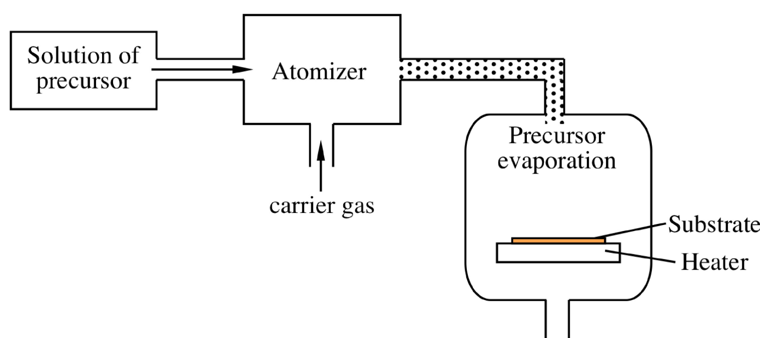

Figure 5.14: Schematic representation of a typical aerosol delivery system for CVD precursors. Adapted from T. T. Kodas and M. J. Hamton-Smith, *The Chemistry of Metal CVD*, VCH, New York (1994).

5.3.3.2 Thermal CVD reactors

In thermal CVD temperatures as high as 2000 °C may be needed to thermally decompose the precursors. Heating is normally accomplished by use of resistive heating, radio frequency (rf) induction heating, or radiant heating. There are two basic types of reactors for thermal CVD: the hot wall reactor and the cold wall reactor.

A hot wall reactor is an isothermal furnace into which the substrates are placed. Hot wall reactors are typically very large and depositions are done on several substrates at once. Since the whole chamber is heated, precise temperature control can be achieved with correct furnace design. A disadvantage of the hot wall configuration is that deposition occurs on the walls of the chamber as well as on the substrate. As a consequence, hot wall reactors must be frequently cleaned to reduce flaking of particles from the walls which may contaminate the substrates. Furthermore, reactions in the heated gas and at the walls deplete the reactants and can result in feed rate limited growth. Figure 5.15 shows a typical low pressure hot wall CVD reactor.

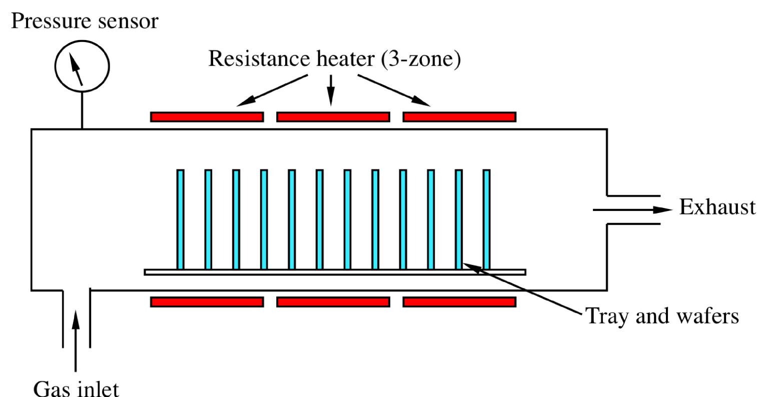

Figure 5.15: Schematic of a typical low pressure hot wall CVD reactor used in coating silicon substrates. Adapted from H. O. Pierson, *Handbook of Chemical Vapor Deposition*, Noyes Publications, Park Ridge (1992).

In a cold wall reactor only the substrate is heated, usually by induction or radiant heating. Since most CVD reactions are endothermic, deposition is preferentially on the area of highest temperature. As a result, deposition is only on the substrate and the cooler reactor walls stay clean. Cold wall CVD has two main advantages over the hot wall configuration. First, particulate contamination is reduced since there are no deposits formed on the walls of the reactor. Second, since decomposition only occurs on the substrate there is no depletion of source gases due to reaction on the walls. However, hot wall reactors tend to have higher throughput since the designs more easily accommodate multiple wafer configurations.

The final issue in design of a thermal CVD reactor is the operating pressure. The pressure of the reactor has a large effect on the rate limiting step of the deposition. Atmospheric pressure reactors have a large boundary layer (Figure 5.10) and non-uniform diffusion of reactants through the boundary layer often results in non-uniform film compositions across the wafer. Conversely, low pressure reactors have a nearly non-existent boundary later and reactants easily diffuse to the substrate (Figure 5.9). However, the difficulty in maintaining a uniform temperature profile across the wafer can result in thickness non-uniformities since the deposition rate in low pressure reactors is strongly temperature dependent. Careful studies of the flow dynamics and temperature profiles of CVD reactors are always carried out in order to achieve uniform material depositions.

5.3.3.3 Plasma-enhanced CVD

Plasmas are generated for a variety of thin film processes including sputtering, etching, ashing, and plasma-enhanced CVD. Plasma-enhanced CVD (PECVD), sometimes called plasma-assisted (PACVD), has the advantage that plasma activated reactions occur at much lower temperatures compared to those in thermal CVD. For example, the thermal CVD of silicon nitride occurs between 700 - 900 °C, the equivalent PECVD process is accomplished between 250 - 350 °C.

A plasma is a partially ionized gas consisting of electrons and ions. Typical ionization fractions of 10^{-5} to 10^{-1} are encountered in process reactors. Plasmas are electrically conductive with the primary charge carriers being the electrons. The light mass of the electron allows it to respond much more quickly to changes in the field than the heavier ions. Most plasmas used for PECVD are generated using a rf electric field. In the high frequency electric field, the light electrons are quickly accelerated by the field but do not increase the temperature of the plasma because of their low mass. The heavy ions cannot respond to the quick changes

in direction and therefore their temperature stays low. Electron energies in the plasma have a Maxwellian distribution in the 0.1 – 20 eV range. These energies are sufficiently high to excite molecules or break chemical bonds in collisions between electrons and gas molecules. The high energy electrons inelastically collide with gas molecules resulting in excitation or ionization. The reactive species generated by the collisions do not have the energy barriers to reactions that the parent precursors do. Therefore, the reactive ions are able to form films at temperatures much lower than those required for thermal CVD.

The general reaction sequence for PECVD is shown in Figure 5.16. In addition to the processes that occur in thermal CVD, reactive species resulting from electron dissociation of parent molecules also diffuse to the surface. The reactive species have lower activation energies for chemical reactions and usually have higher sticking coefficients to the substrate. Therefore, the PECVD reaction is dominated by the reactive species on the surface and not any of the the parent precursor molecules that also diffuse to the surface.

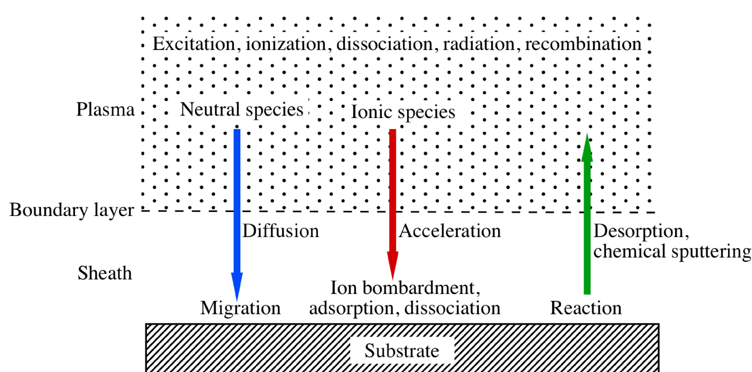

Figure 5.16: Reaction sequence in PECVD. Adapted from M. Konuma, *Film Deposition by Plasma Techniques*, Springer-Verlag, New York (1992).

A basic PECVD reactor is shown in Figure 5.17. The wafer chuck acts as the lower electrode and is normally placed at ground potential. Gases are either introduced radially at the edges of the reactor and pumped out from the center, or gases can be introduced from the center and pumped at the edges as shown in Figure 5.17. The magnetic drive allows rotation of the wafers during processing to randomize substrate position. Some newer reactors introduce the gases through holes drilled in the upper electrode. This method of gas introduction gives a more uniform plasma distribution.

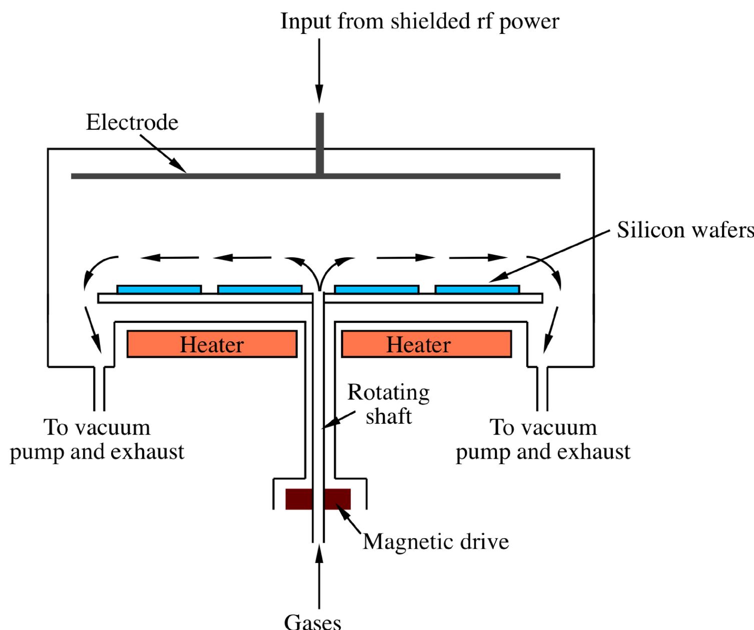

Figure 5.17: Schematic representation of a radial flow PECVD reactor. Adapted from H. O. Pierson, *Handbook of Chemical Vapor Deposition*, Noyes Publications, Park Ridge (1992).

Plasma CVD has numerous advantages over thermal CVD. Obviously the reduced deposition temperature is a bonus for the semiconductor industry which must worry about dopant diffusion and metal interconnects melting at the temperatures required for thermal CVD. Also, the low pressures (between 0.1 - 10 Torr) required for sustaining a plasma result in surface kinetics controlling the reaction and therefore greater film uniformity. A disadvantage of plasma CVD is that it is often difficult to control stoichiometry due to variations in bond strengths of various precursors. For example, PECVD films of silicon nitride tend to be silicon rich because of the relative bond strength of N_2 relative to the Si-H bond. Additionally, some films may be easily damaged by ion bombardment from the plasma.

5.3.3.4 Photochemical CVD

Photochemical CVD uses the energy of photons to initiate the chemical reactions. Photodissociation of the chemical precursor involves the absorption of one or more photons resulting in the breaking of a chemical bond. The most common precursors for photo-assisted deposition are the hydrides, carbonyls, and the alkyls. The dissociation of dimethylzinc by (5.2), a photon creates a zinc radical and a methyl radical ($\cdot CH_3$) that will react with hydrogen in the reactor to produce methane.

$$Zn(CH_3)_2 + h\nu\,(6.4\,\text{eV}) + H_2 \rightarrow Zn + 2\,CH_4 \quad (5.2)$$

Like several metal-organics, dimethylzinc is dissociated by the absorption of only one UV photon. However, some precursors require absorption of more than one photon to completely dissociate. There are two basic configurations for photochemical CVD. The first method uses a laser primarily as a localized heat source. The second method uses high energy photons to decompose the reactants on or near the growth surface.

In thermal laser CVD, sometimes referred to as laser pyrolysis, the laser is used to heat a substrate that absorbs the laser photons. Laser heating of substrates is a very localized process and deposition occurs

selectively on the illuminated portions of the substrates. Except for the method of heating, laser CVD is identical to thermal CVD. The laser CVD method has the potential to be used for direct writing of features with relatively high resolution. The lateral extent of film growth when the substrate is illuminated by a laser is determined not only by the spot size of the laser, but by the thermal conductivity of the substrate. A variation of laser pyrolysis uses a laser to heat the gas molecules such that they are fragmented by thermal processes.

Photochemical effects can be induced by a laser if the precursor molecules absorb at the laser wavelength. UV photons have sufficient energy to break the bonds in the precursor chemicals. Laser-assisted CVD (LACVD) uses a laser, usually an eximer laser, to provide the high energy photons needed to break the bonds in the precursor molecules. Figure 5.18 shows two geometries for LACVD. For the perpendicular illumination the photochemical effects generally occur in the adsorbed adlayer on the substrate. Perpendicular irradiation is often done using a UV lamp instead of a laser so that unwanted substrate heating is not produced by the light source. The parallel illumination configuration has the benefit that reaction by-products are produced further from the growth surface and have less chance of being incorporated into the growing film. The main benefit of LACVD is that nearly no heat is required for deposition of high quality films.

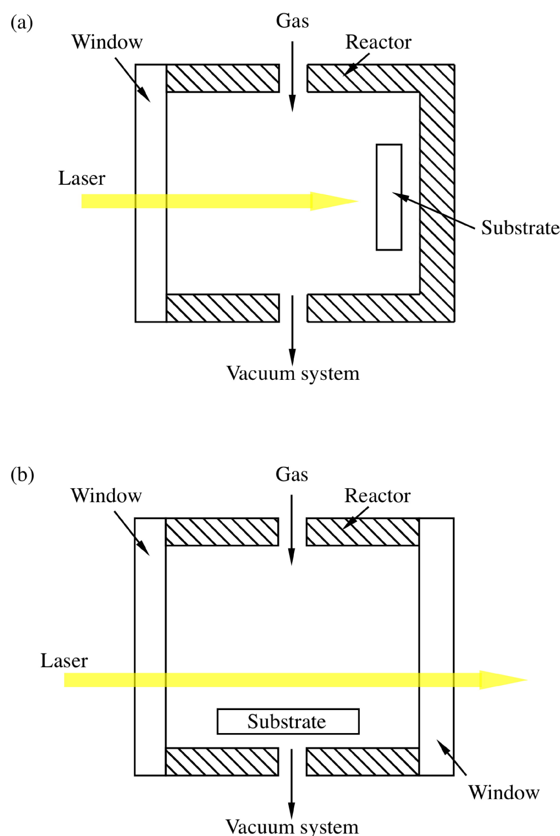

Figure 5.18: Parallel (a) and perpendicular (b) irradiation in laser CVD. Adapted from J. G. Eden, in *Thin Film Processes II*, Eds. J. L. Vossen and W. Kern, Academic Press, New York (1991).

An application of laser photolysis is photonucleation. Photonucleation is the process by which a chemisorbed adlayer of metal precursors is photolyzed by the laser to create a nucleation site for further growth. Photonucleation is useful in promoting growth on substrates that have small sticking coefficients for gas phase metal atoms. By beginning the nucleation process with photonucleation the natural barrier to surface nucleation on the substrate is overcome.

5.3.4 Bibliography

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5.4 Liquid Phase Deposition[4]

5.4.1 Introduction

Silicon dioxide (silica, SiO_2) has been the most researched chemical compound apart from water. Silica has been used throughout history, for example, flint, which when sharpened formed one of humanities first tools. Crystalline silica, or sand, was melted into glass as early as 5000 B.C., birthing a technology that has gained sophistication in modern times. Silicon is the second most plentiful element in the Earth's crust, the most plentiful being oxygen. It is thus surprising that it was not until 1800 that silica was named a compound by Sir Humphry Davy. He, however, failed to isolate its components via electrolysis, and it is Jöns Jacob Berzelius who is thus credited with discovering silica in 1824. He heated potassium fluorosilicate with potassium metal and, after purifying the product of this reaction with water, produced amorphous silica powder.

The most common forms of silica employed in industry include α-quartz, vitreous silica, silica gel, fumed silica and diatomaceous earth. Synthetic quartz is hydrothermally grown from a seed crystal, with aqueous NaOH and vitreous SiO_2, at 400 °C and 1.7 kbar. Because it is a piezoelectric material, it is used in crystal oscillators, transducers, pickups and filters for frequency control and modulation. Vitreous silica is super cooled liquid silica used in laboratory glassware, protective tubing sheaths and vapor grown films. Silica gel is formed from the reaction of aqueous sodium silicate with acid, after which it is washed and dehydrated. Silica gel is an exceptionally porous material with numerous applications including use as a dessicant, chromatographic support, catalyst substrate and insulator. Pyrogenic or fumed silica is produced by the high temperature hydrolysis, in an oxyhydrogen flame, of $SiCl_4$. Its applications include use as a thickening agent and reinforcing filler in polymers. Diatomaceous earth, the ecto-skeletons of tiny unicellular marine algae called diatoms, is mined from vast deposits in Europe and North America. Its primary use is in filtration. Additional applications include use as an abrasive, insulator, filler and a lightweight aggregate.

Methods of colloidal growth and thin film deposition of amorphous silica have been investigated since 1925. The two most common and well-investigated methods of forming SiO_2 in a sol or as a film or coating are condensation of alkoxysilanes (known as the Stober method) and hydrolysis of metal alkoxides (the Iler or dense silica [DS] process).

[4]This content is available online at <http://cnx.org/content/m29774/1.1/>.

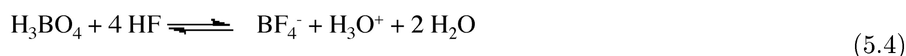
5.4.2 Liquid phase deposition (LPD)

LPD is a method for the "non-electrochemical production of polycrystalline ceramic films at low temperatures." LPD, along with other aqueous solution methods [chemical bath deposition (CBD), successive ion layer adsorption and reaction (SILAR) and electroless deposition (ED) with catalyst] has developed as a potential substitute for vapor-phase and chemical-precursor systems. Aqueous solution methods are not dependent on vacuum systems or glove boxes, and the use of easily acquired reagents reduces reliance on expensive or sensitive organometallic precursors. Thus, LPD holds potential for reduced production costs and environmental impact. Films may be deposited on substrates that might not be chemically or mechanically stable at higher temperatures. In addition, the use of liquid as a deposition medium allows coating of non-planar substrates, expanding the range of substrates that are capable of being coated. Aqueous deposition techniques have not reached the level of maturation that vapor-phase techniques have in respect to a high level of control over composition, microstructure and growth rates of the resulting films, but their prospect makes them attractive for research.

LPD generally refers to the formation of oxide thin films, the most common being SiO_2, from an aqueous solution of a metal-fluoro complex $[MF_n]^{m-n}$, which is slowly hydrolyzed using water, boric acid or aluminum metal. Addition of water drives precipitation of the oxide. Boric acid and aluminum work as fluoride scavengers, rapidly weakening the fluoro complex and precipitating the oxide. These reactants are added either drop wise or outright, both methods allowing for high control of the hydrolysis reaction and of the solution's supersaturation. Film formation is accomplished from highly acidic solutions, in contrast to the basic or weakly acidic solutions used in chemical bath deposition.

A generic description of the LPD reaction is shown in (5.3), where m is the charge on the metal cation. If the concentration of water is increased or the concentration of hydrofluoric acid (HF) is decreased, the equilibrium will be shifted toward the oxide. Use of boric acid or aluminum metal will accomplish the latter, see (5.4) and (5.5). The most popular of these methods for accomplishing oxide formation has been through the addition of boric acid.

(5.3)



(5.4)

(5.5)

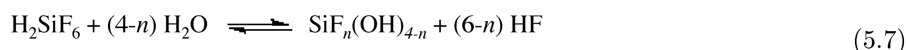
The first patent using liquid phase deposition (LPD) of silicon dioxide via fluorosilicic acid solutions (H_2SiF_6) was granted to the Radio Corporation of America (RCA) in 1950. RCA used LPD as a method for coating anti-reflective films on glass, but the patent promised further applications. Since this initial patent there have been many further patents and papers utilizing this method, in variable forms, to coat substrates, usually silicon, with silicon dioxide. The impetus behind this work is to create an alternative to the growth of insulator coatings by thermal oxidation or chemical vapor deposition (CVD) for planar silicon chip technology. Thermal oxidation and CVD are performed at elevated temperatures, requiring a higher output of energy and more complicated instrumentation than that of LPD. The most simple and elegant of the LPD methods uses only water to catalyze silica thin film growth on silicon from a solution of fluorosilicic acid supersaturated with silicon dioxide, (5.6).

(5.6)

The amount of water reacted with the supersaturated fluorosilicic acid solution controls both the growth rate and incorporation of fluorine into the resulting silica matrix. Both growth rate and fluorine content increase with increased addition of water. Ultimately this "dilution" affects the optical properties of the resulting silica film; an increased amount of fluorine decreases its dielectric constant (and thus its refractive index).

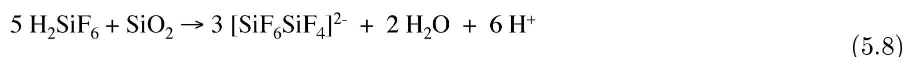
To ensure a uniform film growth with LPD, the preparation of the surface to be coated is of utmost importance. Suitable treatments may involve the formation of surface hydroxides, the pre-deposition or self-assembly of an appropriate seed layer. The most efficient coverage is seen with silicon surfaces functionalized with hydroxy (-OH) groups prior to immersion in the growth solution. This can be achieved through appropriate etching of the silicon surface. It is proposed that the silanol (Si-OH) groups act to seed the growth of the silica film through condensation reactions with the silicic acid formed in the growth solution.

Lee and co-workers and Homma separately propose that intermediate, hydrolyzed species, $SiF_n(OH)_{4-n}$ ($n < 4$), are formed by the reaction shown in (5.7). According to Lee, these species then react with the substrate surface to form a film. Homma proposes that fluorine-containing siloxanes are subsequently formed, which adsorb onto the surface where condensation and bonding occurs between the oligomers and surface hydroxyl groups. The former mechanism implies a molecular growth mechanism, whereas the latter implies homogeneous nucleation with subsequent deposition.



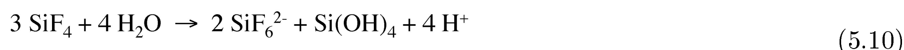
$$H_2SiF_6 + (4\text{-}n)\, H_2O \rightleftharpoons SiF_n(OH)_{4-n} + (6\text{-}n)\, HF \tag{5.7}$$

In concentrated fluorosilicic acid solutions silica can be dissolved to well beyond its solubility, forming fluorosilicon complexes such as $[SiF_6.SiF_4]^{2-}$, (5.8). The bridged fluorosilicon complex has electron deficient silicon because of the high electronegativity of the bonded fluorines, creating weak Si-F bonds. These bonds are then prone to nucleophilic attack by water. The fluorine ion (F^-) combines with the proton in this reaction to form hydrofluoric acid (HF). The product of this reaction can then react further with water to yield $[SiF_4(OH)_2]^{2-}$, SiF_4 and HF. The high acidity of the solution then allows protons to react with $[SiF_4(OH)_2]^{2-}$ to form tetrafluorosilicate (SiF_4) and water, (5.9). Hydrolysis of the SiF_4 will then yield the hexafluorosilicate anion, protons and silicic acid, (5.10).



$$5\, H_2SiF_6 + SiO_2 \rightarrow 3\, [SiF_6SiF_4]^{2-} + 2\, H_2O + 6\, H^+ \tag{5.8}$$

$$[SiF_4(OH)_2]^{2-} + 2H^+ \rightarrow SiF_4 + 2\, H_2O \tag{5.9}$$



$$3\, SiF_4 + 4\, H_2O \rightarrow 2\, SiF_6^{2-} + Si(OH)_4 + 4\, H^+ \tag{5.10}$$

Silicic acid is adsorbed onto the surface of the substrate that has been introduced into the growth solution. Molecular growth of silica on the substrate surface is initialized in an acid catalyzed dehydration between the silicic acid and the silanol groups on the substrate surface. Si-O-Si bonds are formed, resulting in an initial silica coating of the surface. Following reactions between the initial silica coating and the monosilicic acid in solution result in further silica deposition and growth. Because of the presence of HF in the solution, the surface and growing silica matrix is subject to attack according to the reaction in (5.11). This explains the incorporation of a quantity of fluorine into the silica film. Additionally, it reveals that a certain amount of silica etching occurs along with growth. Because of the prevalence of the silicic acid in the solution, however, deposition is predominant.

$$Si\text{-}OH + HF \rightarrow Si\text{-}F + H_2O \tag{5.11}$$

This proposed mechanism, which is more in depth than those proposed by Lee and Homma, elucidates what is experimentally proven. The deposition rate of the silica increases with addition of H_2O because the nucleophilic attack of the fluorosilicon complex is then augmented, increasing the concentration of silicic acid in the growth solution. The H_2O addition increases the reaction rate and thus the concentration of HF in the growth solution, resulting in greater incorporation of fluorine into the silica matrix because of HF attack of the deposited film. Additionally, Yeh's mechanism supports a molecular growth model, i.e., heterogeneous growth, which represents a consensus of the body of research performed thus far.

In a solution with dissolved ceramic precursors, nucleation and growth will occur either in solution (homogenous nucleation) or on the surfaces of introduced solid phases (heterogeneous nucleation). Successful

film formation relies on the promotion of heterogeneous nucleation. Solubility generally depends on the solution pH and the concentration of the species in solution. As the solution crosses over from a solvated state to a state of supersaturation, film formation can occur. It is vital to assure that the state of supersaturation is one that promotes film growth and not homogeneous nucleation and precipitation. This concept is illustrated in Figure 5.19.

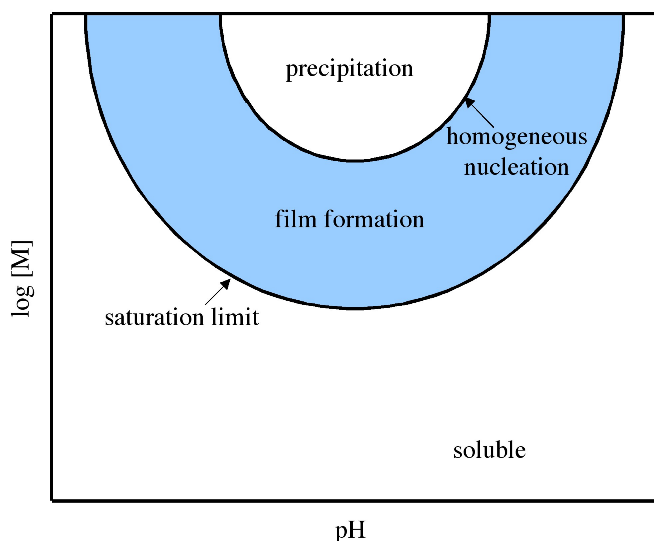


Figure 5.19: Idealized solubility diagram for film forming species in water. Adapted from B. C. Bunker, P. C. Rieke, B. J. Tarasevich, A. A. Campbell, G. E. Fryxall, G. L. Graff, L. Song, J. Liu, J. W. Virden, and G. L. McVay, *Science*, 1994, **264**, 48.

Silica can be dissolved in fluorosilicic acid to well above its solubility in water, which is approximately 220 ppm (mg/L). Depending on the concentration of the fluorosilicic acid solution, it can contain up to 20% more silica than is implied by the formula H_2SiF_6. After saturation of the solution with SiO_2, the solvated species is a mixture of fluorosilicates, which reacts as explained earlier. It must be emphasized that addition of water in this reaction is not simply dilution, but is the addition of a reactant, which places the solution in a metastable state (the blue area in Figure 5.19) in preparation for the introduction of a suitable surface to seed the growth of silica.

Another important factor in solution growth methods is interfacial energy. When a substrate with lower interfacial energy than that of a growing homogeneous nucleus is introduced into a growth solution, heterogeneous growth is favored. Thus, a seeded growth mechanism by definition introduces a substrate of lower interfacial energy into a supersaturated solution, facilitating heterogeneous growth. Lower interfacial energies can be a product of surface modification, as well as a property of the materials' natural state.

5.4.2.1 Comparing LPD to sol-gel

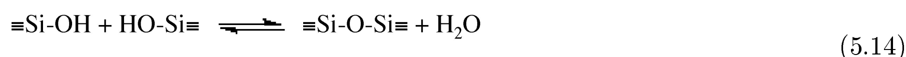
An alternative method to LPD for forming silica thin films is the sol-gel method. A sol is a colloidal dispersion of particles in a liquid. A gel is a material that contains a continuous solid matrix enclosing a continuous liquid phase. The liquid inhibits the solid from collapsing and the solid impedes release of the liquid. A formal definition of sol-gel processing is the "growth of colloidal particles and their linking together to form

a gel." This method describes both the hydrolysis and condensation of silicon alkoxides and the hydrolysis and condensation of aqueous silicates (the DS process).

In the hydrolysis of silicon alkoxides, an alkoxide group is replaced with a hydroxyl group, (5.12). Further condensation reactions between alkoxyl groups or hydroxyl groups produce siloxane bonds, see (5.13) and (5.14).

(5.12)

(5.13)


(5.14)

Tetramethoxysilane [$Si(OMe)_4$, TMOS] and tetraethylorthoxysilane [$Si(OEt)_4$, TEOS] are the most commonly used precursors in silica sol-gel processing. The alkoxides are hydrolyzed in their parent alcohols, with a mineral acid or base catalyst, producing silicate gels that can be deposited as coatings. The Stober method, which utilizes this chemistry, relies on homogeneous nucleation to produce monodisperse sols.

Iler's DS method of silica film formation was originally patented as a pigment coating to increase dispersibility of titania particles for use in the paint industry. The DS method is based on the aqueous chemistry of silica and takes advantage of the species present in solution at varying pH. Below pH 7 three-dimensional gel networks are formed. Above pH 7 silica surfaces are quite negatively charged ((5.15)), so that particle growth occurs without aggregation. The isoelectric point of silica is pH 2. Reactions above and below pH 2 are thought to occur through bimolecular nucleophilic condensation mechanisms. Above pH 2 an anionic species attacks a neutral species ((5.16)) and below pH 2 condensation involves a protonated silanol ((5.17)). The DS process has been utilized extensively in sol-gel coating technology and as a growth method for monodisperse and polydisperse sols.

(5.15)

(5.16)

(5.17)

5.4.3 Bibliography

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