

Appendix A

Introduction

Advances in science often pave the way for significant advances in technology. The advent of modern integrated circuits in the electronic devices widely adopted by our digitally obsessed society would not have been possible without the development of the science of thin films. The dawn of the thin solid films have made available the portability of the devices we covet. However, the age of the thin film would not have come to pass without the advent of the chemical vapor deposition process (CVD) process. At the most basic level, CVD is the deposition of a solid on a heated surface from a chemical reaction in the gas phase³.

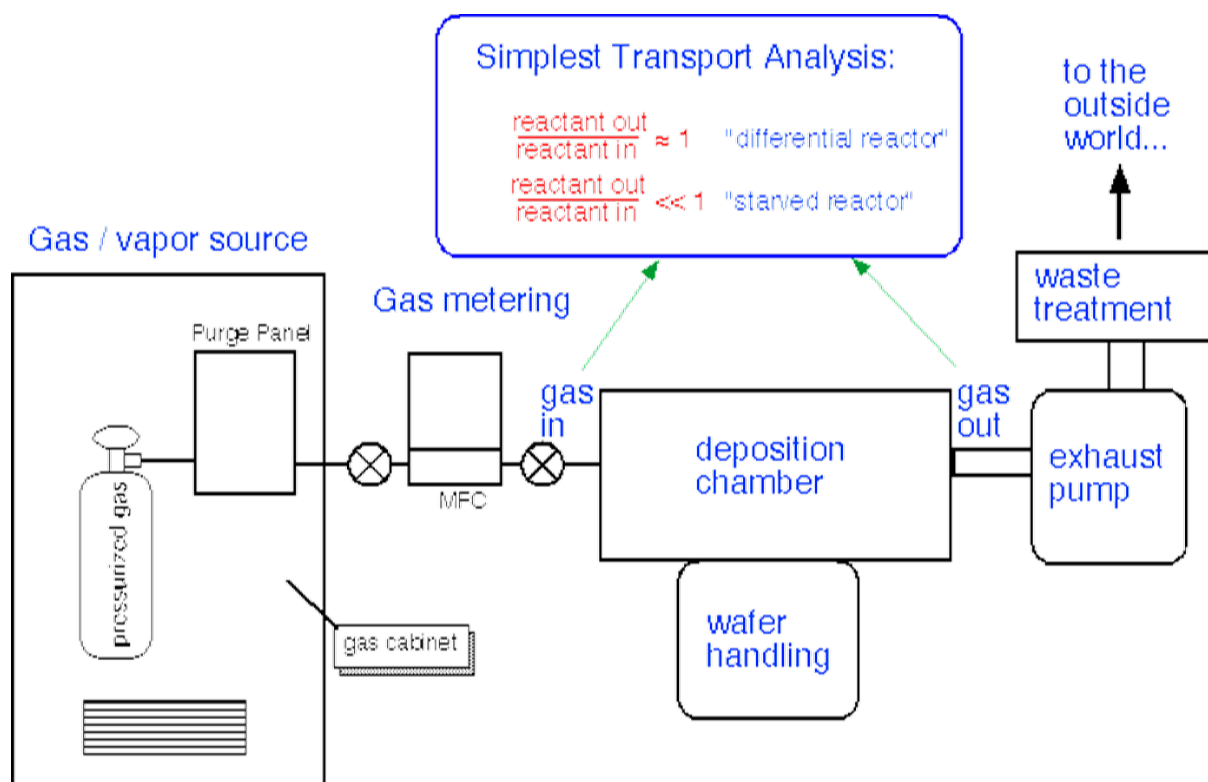


Figure 1-Depiction of a generic CVD reactor showing major system level components¹⁶.

Generally, CVD falls into a category of material transfer process that tends to be atomistic in constitution. Other common vapor transport techniques include physical vapor deposition and atomic layer deposition, with each process continuing unique advantages and disadvantages^{3, 10}. The reason chemical vapor deposition is the focus of this paper is to outline the distinct advantages of CVD over other techniques and briefly summarize the fundamental concepts essential to its employment in scientific and industrial settings.

Background

CVD is often the method of choice in semiconductor fabrication and material coating processes. This is due to the high throwing power or conformality CVD offers over other vapor transport techniques. Throwing power refers to the ability of a process to coat surfaces orthogonal to the direction of gas flow. Complex surface topographies and detailed three-dimensional structures can often be evenly covered with CVD where other methods of vapor transport are strictly limited to line of sight deposition. An example of the superior conformality of CVD, involves tungsten deposition on integrated circuits. The circuits often contain deep holes with aspect ratios approaching 10:1. Another positive attribute of CVD is the high deposition rate and thick coatings obtained. Hundreds of microns or in extreme cases centimeter thick coating can be achieved using CVD. In contrast, PVD films are generally limited to much thinner layers and require considerably longer deposition times^{3,9,10}.

Versatility is unique to CVD, in that it can be performed over a variety of pressure regimes. Most treatments are application specific, but CVD is common at both low and atmospheric pressures. Low pressure CVD (LPCVD) can loosely defined as deposition below atmospheric pressure to 10^{-7} mbar³. Deposition below 10^{-7} mbar is referred to as ultra-high vacuum CVD (UHVCVD) and is much more specific in application. Atmospheric pressure, (APCVD), and LPCVD predominate in most applications. This broad range in pressure is an advantage from the standpoint of required equipment. In most cases, Ultra –high vacuum equipment and methodologies are not required. This is not the case in PVD and ALD, as both of these techniques require pressures below 10^{-7} mbar to achieve desired results. Fundamentally, the advantages of CVD translate to cost savings in industry. If high quality coating can be performed at a variety of pressures in a short time, the more productivity and throughput can be achieved.

With that said, there are advantages of CVD that need to be addressed in order to fully appreciate the process. Perhaps the biggest problem with CVD is the requirement to have precursors in the gas phase¹⁰. This somewhat limits what can be deposited using this method, as not all desired semiconductors or metals have suitable gas or high vapor pressure liquid precursors. To compound the problem, most of the gases and liquids that meet the criteria for good CVD precursors are hazardous, corrosive and toxic. Furthermore, the byproduct of the reactions inherent to CVD is also hazardous which can lead to high operating costs to address the nature these materials.³ Secondly, effective CVD employs some form heating method to break down the precursors into the desired components. Therefore, CVD is essentially most effective at temperatures above 600 °C. The resultant problem is that not all substrate materials are stable at elevated temperatures⁵.

Preliminary Considerations

The first step in any chemical vapor deposition should begin with an appropriate theoretical investigation into the reaction being considered¹⁰. This analysis will help establish boundary conditions for the proposed reaction, identify reactive intermediate and potential by-products, determine a viable reaction mechanism, expected stoichiometry and the resultant deposition structure⁹. The intention of the analysis is to narrow the scope of the process and save a great deal of time and cost later in the process. The hallmark of a good theoretical analysis begins with a brief treatment of the fundamental thermodynamics applicable to the desired reaction. The Gibbs free energy of formation (ΔG_f) is a perfect starting point in that it predicts whether or not a chemical reaction will occur. The Gibbs free energy of formation is defined as the ΔG of the products minus the reactants:

$$\Sigma \Delta G_r^\circ = \Sigma \Delta G_f^\circ \text{products} - \Sigma \Delta G_f^\circ \text{reactants}$$

The Gibbs number is not a fixed value, but depends on a number of parameters including the reactant types the molar ratio, temperature and pressure. The Ellingham diagram is a useful tool for CVD because it graphically depicts the thermodynamic feasibility of a reaction³. This allows the user to determine quickly if the considered reaction is plausible in a set of prior determined boundary conditions.

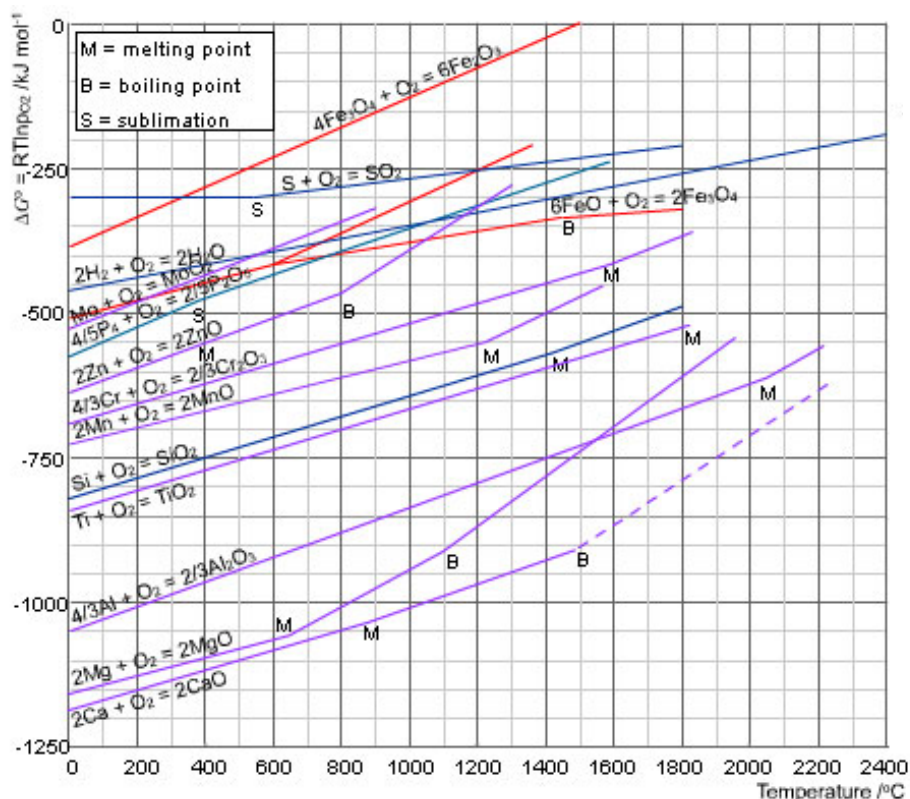


Figure 2-Image of Ellingham diagram of ΔG formation of metal oxides verses temperature¹⁷

So far, the thermodynamics as they apply to CVD have been simplified. For a complete treatment of the thermodynamics of proposed reaction, a Gibbs free energy equilibrium calculation is often required to yield the most data about possible intermediates and phases possible in the reaction. These calculations scale with system parameters and become lengthy and arduous depending on the number of species involved. Computer simulation is often employed to simplify this process. These computer codes work by determining chemical equilibrium by minimizing the Gibbs free energy^{5,10}. Variables such as temperature, volume and pressure are constants in these calculations. The resultant data garnered from the calculation is useful in CVD as it can provide insight into the chemical composition and expected amounts of deposited material under the user established boundary conditions, the existence of gas species formed during the reaction, the likelihood of additional reactions or phase transitions. Lastly, theoretical analysis can predict compatibility of the proposed substrate material with gaseous species in the reactor. These considerations are important from a planning perspective in that they provide insight into overall reactor design and necessary chemical safety systems. Despite the increased reliance modeling and simulation over the years, theoretical data is not a viable substitute for experimental observation, and a thorough literature search should be conducted on the topic of interest further plan the proposed CVD process.

Transport

An integral part aspect of chemical or physical vapor deposition processes involves transport of species from one place to another. In the case of CVD, this more specifically refers to the movement of the precursors from the inlet to the substrate surface where deposition can take place. This mass transport becomes a primary consideration in the early stages of CVD process development because the dynamics of mass transport govern the rate at which deposition can proceed. There are two common regimes to CVD in terms of transport phenomenon. The first describes a scenario commonly encountered in smaller lower throughput reactors and yields a deposition rate proportional to the surface reaction rate. This regime is referred to as surface limited regime and is met when reactor scale is biased in the favor of gas flow. In the opposite mass transport limited scenario, the reactor is load limited and the limiting step is the process of applying enough precursors to adequately cover the substrates being deposited. It becomes obvious why the latter is often experienced in commercial CVD reactors, where throughput is a primary concern.

Transport is all encompassing term and a better understanding can be gained when looking at the individual quantitative components of transport. The first topic to be addressed under transport is the concept of flux. Flux is the product of the velocity of a fluid and the density with respect to time⁴. Mathematically, flux is represented by the equation below:

$$J = nu$$

where n is molecular concentration and U is velocity. The velocity portion of the equation is a vector quantity and therefore flux is also a vector. These quantities can be expressed in a variety of units; $\text{kg/m}^2 \text{ sec}$, $\text{moles/m}^2 \text{ sec}$ are both equally valid if used consistently in calculations. Simple integration of the flux over a known area allows one to determine the total amount of material transferred across said surface. This is useful in allowing a quick determination of the amount of material across the substrate and can help with identification of transport limited scenarios^{5,10}.

Like the molecular flux, convection and diffusion play important roles in understanding general transport in CVD processes. Convection is a type of flux, and refers to the overall movement of the fluid in the system. A more specific method of transport is diffusion and is more narrowly defined. Diffusion specifically refers to the motion of the fluid from thermal sources, internal or external. Drastic differences in the movement of fluid in the system can result from diffusion processes. Differences in temperature as well as concentration can move the fluid in the system toward an equilibrium condition. The flux as it relates to concentration gradient is given by:

$$J = -D \frac{d_n}{d_x}$$

The quantity $\frac{d_n}{d_x}$ is the gradient in concentration of the fluid species and D is the diffusion constant. The negative value on the diffusion constant indicates the diffusion always occurs down the gradient or areas from higher to lower concentration. In this expression, the units of D are given in units of $\text{length}^2/\text{time}$. The value of D , can be estimated by:

$$D \sim \sqrt{\frac{k^3}{\pi^3 m} \frac{T^{3/2}}{P a^2}}$$

where k is Boltzmann's constant, T is the absolute temperature, m is the mass, P is the system pressure, and a is the radius of the atom or molecule. This approximation is commonly referred to as the hard sphere approximation and assumes that the fluid is comprised of hard spheres of equal size and mass. For most commonly countered CVD problems, this approximation is an adequate representation of process transport in a binary mixture¹².

Expanding on the idea of diffusion, the diffusion length is a useful tool in understanding the overall fluid transport. The diffusion length (dl) refers to the specific length scale for system diffusion. The dl scales with the square root of time. For practical CVD design considerations, if the dl is considerably longer than the reactor size, the profile concentrations will be linear and time independent; thus transport is diffusion dominated. However, if the calculated diffusion length is much shorter than system size, fluid concentrations can significantly vary in specific

regions of the system. This can lead to large concentration gradients that are time dependent. This can lead to a starved situation if the given system length is short enough ⁸.

One useful tool in the CVD handbook is to calculate the Peclet number for the system¹². The Peclet number is the ratio of system length and the diffusion length as a function of the residence time of the fluid being examined. In this case, the residence time of is simply the average time the precursors spend in the reactor ¹⁰. This notion is important because a laconic residence time will not allow sufficient time for deposition to transpire, thus leading to a starved reactor scenario. The Peclet number is dimensionless number defined by the following equation:

$$P_e = \frac{LU}{D}$$

V is the velocity of the fluid, L is the characteristic length of the system and D is mass diffusion coefficient.

Another dimensionless number that is also of use in chemical vapor deposition is the Reynolds number. The Reynolds number describes the flow behavior of the fluid in the chamber. The two types of flow commonly encountered in CVD are laminar and turbulent flow. In the case of laminar flow, the gas velocity on the inner wall of the CVD reactor is zero. For simplicity, this is assumed a tube. This leads to the formation-defined boundaries in the total flow. The boundary formation begins at the fluid entrance at the tube and increases in thickness until the fluid is stabilized by system parameters⁸.

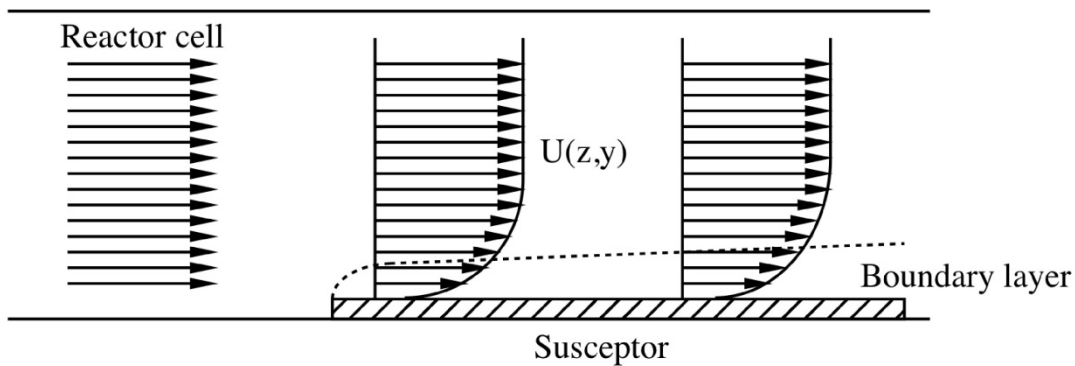


Figure 3-Image of a tube reactor showing laminar flow and boundary layer formation⁸

Mathematically, the Reynolds (R_e) number is the mass density times the flow density divided by the viscosity of the fluid.

$$R_e = \frac{\rho \mu_x}{\mu}$$

Reynolds number values allow the user to describe the relative amount of gas flow. For R_e values > 2200 , the flow is always turbulent and R_e values < 1200 indicate viscous flow⁸. When the R_e is above 1200, but below 2200, either regime can exist, but is defined by specific system configuration, such as the placement of inlet and respective outlets as well as piping complexities. One can assume that the boundary layer thickness increases with lower gas-flow velocity and with increased distance from the tube inlet. Additionally, the thickness of the boundary layer (Δ) can be determined by the square root of the distance from the inlet in the direction of flow divided by the Reynolds number.

$$\Delta = \sqrt{\frac{x}{R_e}}$$

This is helpful in determining applicable flows based on system dimensions.

The last dimensionless number helpful to the depositor is the Knudsen number (Kn). In order to utilize the Knudsen relationship, the mean free path (λ) must be known or approximated⁸. The mean free path refers to the distance the respective gas particles travel in a system before encountering another particle. It is defined in the kinetic theory of gases as:

$$\lambda = \frac{1}{2^{1/2} \pi d_0^2 n},$$

where d_0 is the molecular diameter in meters and n is the gas density in molecules per cubic meter. The mean free path (λ) is both gas density and pressure dependent at a given constant temperature. The Knudsen number,

$$Kn = \frac{\lambda}{d}$$

is simply the mean free path divided by a characteristic length (d). In the simplified tubular reactor model currently being employed, this would simply be the tube diameter.

In contrast to the Reynolds number that describes relative flow, the Knudsen number characterizes the nature of the gas in a system. Together, the Knudsen and Reynold's numbers can be used to characterize the constitution of the gases and the type of flow in the system.

Three common natures of gases in a system are viscous, molecular and transitional. A viscous gas is characterized by a $Kn < 0.01$ which also marks the continuum flow regime. At $Kn < 0.01$, the diameter of the tube is much greater than the mean free path for collisions, and gas flow is determined by gas-gas collisions. At high pressures, the viscous region predominates.

Continuum flow can be either turbulent or laminar viscous as determined by the Reynolds number. A good example of turbulent gas flow would be smoke billowing from a stack. In laminar flow, the behavior of the gas is ordered, and resembles a defined stream⁸. See figure four for a visual comparison of both turbulent and laminar flow. At $Kn > 10$, the mean free path

between gas-gas collisions is much greater than the tube diameter and here gas molecules move freely until they interact with the wall. Under these conditions, the gas begins to behave less like a collective fluid and more like individual molecules; thus, giving the term molecular flow. In this region, the mean free path has increased to the point that the dominant interaction of the gas is not particle-particle collisions, but rather particle- wall collisions. For Knudsen values $\gg 1$, the gas will exhibit viscous behavior and gross approximations are valid. At Knudsen values $\ll 1$, it becomes necessary to model individual molecular trajectories in the system via Monte Carlo techniques^{8, 10}.

The concept of fluid flow can become increasingly complex when system design includes flow spanning several pressure regions. The area between viscous flow and molecular flow is known as the transition flow region. It typically dominates from pressures 1 mbar to 10^{-3} mbar. At this flow, the mean free path approximates the diameter of the system. A common trait of most CVD system is to operate a variety of pressures and therefore one can assume different flow regimes. Ideally, chemical vapor deposition is preferred in the viscous flow regime with Re values < 1200 and Kn values < 0.01 ⁶.

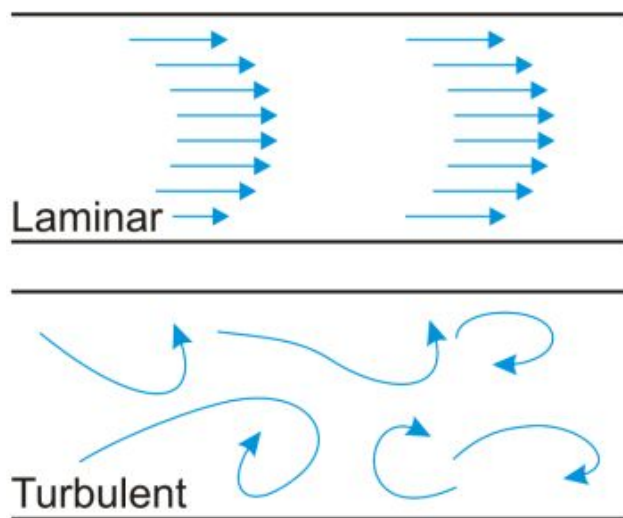


Figure 4-Image comparison of turbulent and laminar flow¹⁸

To this point, the discussion of transport in CVD has focused on methods and ideas of mass transport of fluids. This is by no means an exhaustive treatment on this topic but provides an overview of some of the tools for effective CVD. However, heat transport is also paramount in understanding the CVD process. Heat transport is so fundamental in CVD that it often defines

the term for the type of CVD being employed. In CVD processes where the sample is the only object being heated, these are referred to cold-wall reactors.¹⁰ In contrast, experiments where the whole chamber is heated are called hot-wall¹⁰. Each process has its own distinct advantages and disadvantages. The decision really comes down to the specific chemistry involved in the CVD, which will be discussed later.

There are three primary modes of heat transport in CVD that need to be considered. The first is conduction. Heat conduction is the motion of heat through a media (solid, liquid, gas). In a CVD reactor this happens by mass transport⁵. Diffusion can be an important mechanism of heat conduction and can be treated with the same rigor as seen in diffusion of fluids. Another method of heat transport is convection. Here, heat is transferred to the substrate by the physical movement of gases or liquids. Convection, like conduction, can still be approximated using the diffusion formulas by assuming the diffusion is bounded to streamlines like those observed in laminar fluid flow^{5,12}. The last method of heat transport is radiative transport. This method dominates in vacuum and occurs via the movement of photons from a source to an object. Radiative transport is surprisingly effective, particularly at high temperatures, but even the smallest amount of gas between the source and the object can induce conduction, which can lead to unanticipated spikes in temperature which are potentially catastrophic to CVD processes.

Like fluids, heat transport can be accurately described in terms of a flux³. For heat bounded by conduction, the heat flux is

$$q = -k \frac{dT}{dx}$$

where T is the temperature and k is the thermal conductivity, a material specific quantity describing the rate at which heat flows within a body. The units of k are W/(m•K). Heat flow follows a gradient; the negative sign indicates it flows from areas of higher temperature to lower. Thermal conductivity can vary widely in differing materials and the conductivity of materials in the reaction zone need to be carefully considered to achieve optimum results.

One useful tool in heat transport calculations that can be employed is the Rayleigh number. This dimensionless quantity, similar to the dimensionless numbers used to characterize fluid flow will indicate the presence and magnitude of natural convection in a system. Systems dominated by natural convection can have significant deleterious effects. Gas recirculation, excessive powder formations from increased residence times are all possible with natural convection dominated systems. Ideally, the forced convection from flow injectors is sufficiently high to negate natural convection processes. Since natural convection is influenced by system length, a good rule of design is keep the reactor distance from the fluid injectors as short as possible.

In stark contrast to conduction and convection, radiative heat transfer has no correlative in mass transport since it solely depends on the movement of photons. Thermal radiation is an important topic to consider in CVD since many system employ it has the source of heat in the reactor.

Radiation offers distinct advantages to both convection and conduction in that it offers a non-contact method to heat a substrate. This is often the best-case scenario in device fabrication and detailed CVD processes because the reduced potential from interference in precursor flow and deposition. At a high level, thermal radiation can be quantitatively described using the *Stefan-Boltzmann law*, which relates the energy from a blackbody to the fourth power of the temperature. since it solely depends on the movement of photons. In order to estimate the impact of temperature from photon impingement, a relationship must be established.

$$e_b = \sigma T^4$$

In the above equation, the σ term is the Stefan-Boltzmann constant with a value of $5.669 \times 10^{-8} \text{ W/(m}^2 \cdot \text{K}^4)$. As stated before, the above equation is only valid for ideal radiators. This is rarely the case in CVD as only small number of materials behave as blackbodies under a set of prescribed conditions, both of which are under flux in typical processes. Therefore, it is necessary to modify the *Stefan-Boltzmann law* to incorporate these non-ideal radiators. The energy from a real material is the product of the emissivity (ϵ) the Stefan- Boltzmann constant and the temperature to the fourth power.

$$e = \epsilon \sigma T^4$$

The material specific emissivity is a surface property and has values between 0.01 and 1, with 1 being a blackbody. Empirically, the emissivity is the ratio of the radiation emitted from a real surface and a blackbody surface at the same temperature.

$$\epsilon = \Phi_r / \Phi_b$$

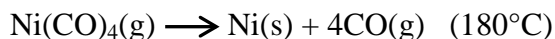
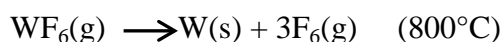
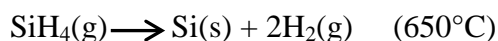
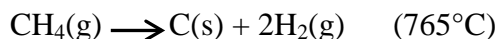
A full treatment of the behavior of radiation in a system can become extremely complex and is out of the scope of this manuscript. However, in most cases of CVD, the heated object is a flat substrate sitting on a heated mass¹². With relatively simple approximations, the heat can be estimated thus eliminating the need for in depth modeling to perform good chemical vapor deposition.

CVD Chemistry

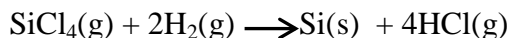
Understanding and controlling the chemistry is fundamental to successful film growth by CVD. Similarly, fundamentals of fluid and heat flow have been addressed because these considerations tend to dominate early planning in reactor design. At a minimum, a cursory knowledge of the chemistry involved is needed to complete a fluid flow analysis. Perhaps the most important aspect in the chemistry of CVD is a thorough understanding of the possible chemical reactions that can occur in the system. Knowledge of the possible chemistry is the key to product quality and guides the selection of critical system parameters such as temperature. A convenient way to

examine CVD chemistry and the way which will be employed here is to describe the most common reaction types employed in CVD reactors to deposit films and coatings.

One of the most widely used reactions in industry is pyrolysis; it is simple, effective, and versatile. In this process, thermal energy is used to split a molecule into its compositional elements. Species such as hydrocarbons, hydrides, halogens, carbonyls and organometallics can all be broken down in this manner to form films and coatings on substrates. Common pyrolysis reactions are shown below^{10,11}.



Reduction is another chemical reaction commonly employed in CVD. It typically involves the introduction of hydrogen to reduce halides, carbonyl halides, or oxyhalides to the desired element. Of all of the possible reactions, the reduction of silicon tetrachloride to single crystal Si is one of the most employed.

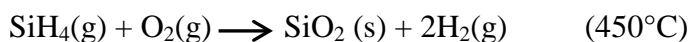


Another reduction reaction common to major production is the reduction of tungsten hexafluoride with hydrogen according to the reaction below:



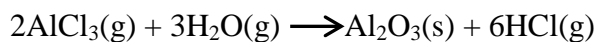
One of the big advantages to the reduction reactions over pyrolysis is that the reactions can typically be carried out at lower temperatures¹⁰. An important note for CVD is reduction does not have to be the primary reaction. Hydrogen can take on a supplementary role in reactions where the prevention of carbides or oxides is desirable. In these reactions, hydrogen will serve as a scarfing agent to preferentially form hydride species that can be more easily removed from the reaction chamber and lessen the impact on film or coating quality⁹.

In some reactions critical to the electronics industry the formation of oxides is the primary goal of the reaction. The reaction of silane with oxygen is a classic example of this reaction, which leads to the formation of high purity silicon dioxide¹⁰.



Elemental oxygen is not the sole source of oxygen in the formation of oxides. Hydrolysis or the introduction of water, can also serve as a powerful oxidizer. Hydrolysis is used less frequently

because in most CVD chemistry, water is not compatible with the desired end product and vigorous steps are used to eliminate water from the reactor. However, in the case of aluminum oxide coating on tool steels, hydrolysis is the preferred method according to the reaction:

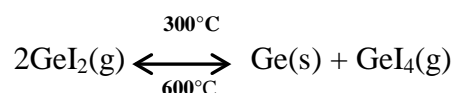


A more general grouping of CVD reactions is compound formation. In this group, a variety of chemistries is employed to deposit different species. Some of the more common reactions falling into this category are carbidization and nitridation reactions where the introductions of carbon or nitrogen respectively form carbides and nitrides. The deposition of borides also falls into this group. These reactions are normally used more in the coatings industry rather than thin film growth. In thin film CVD, product quality is paramount in that the end goal is most likely, a desired electrical property. Electrical properties are adversely affected by morphology; therefore CVD processes need to be more stringently controlled to maintain high quality. In contrast to thin film deposition, the coating industry is mainly focused on bulk properties of the coating and therefore crystal quality is of less importance. A good example of this is the carbide coatings on tool steel for wear resistance.

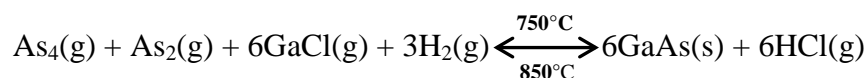
The deposition of carbides usually involves the reaction of a halide with a hydrocarbon. Because of its ubiquitous nature and relatively low decomposition temperature, methane is the precursor of choice for most carbide depositions. Take the reaction of titanium tetrachloride with methane for instance. TiCl_4 will react with CH_4 at 1000 degrees C to form TiC according to the reaction below:



The previously presented reaction types represent some of the most common reactions to the electronics and coatings industry. Therefore, these reactions are well studied and the thermodynamics and kinetics are straightforward. For the sake of completeness, there are a couple of reaction types that are far less common, but nonetheless worth a brief treatment. Ohring⁹ discusses these reactions in the CVD chapter of his thin films text and will be briefly summarized here. The first reaction takes place under a strict set of conditions and only occurs when a nonvolatile metal can form volatile compounds with varying degrees of stability as a function of temperature. This phenomenon is most common to halide chemistries when the metal can exist in two valence states. The high electronegativity of the halides allows this. In most cases, the lower valent metal is more stable with respect to temperature. As a result, the lower valent halide can be transported in the vapor phase to reaction with its respective metal to form the higher valent halide. This has been demonstrated in the halides of Al, B, Ga, In, Si, Ti, Zr, Be, and Cr. An example of this is the disproportionation reaction of germanium diiodide to form germanium tetraiodide and germanium:



The other type of reaction similar to disproportionation is reversible transfer. In reversible transfer, the reaction is characterized by the reversal in the chemical equilibrium at both the source and deposition side of the reactions at different temperatures in the reactor. Consider the formation of GaAs from the chloride as a simplified example of this process.



In this reaction the AsCl_3 serves as the carrier and transports molten Ga toward the substrates in the form of the metal chloride vapor. This in turn reacts with the arsenic to form GaAs at the lower temperature. At the higher temperature, the reverse reaction occurs and the film is etched leading to net removal of gallium⁹.

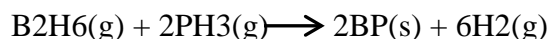
Now that the most common reaction types in CVD have been addressed, the focus will shift to examine the precursors themselves. An important aspect to high quality CVD is the selection of the proper chemistry to maximize the end product. In the reactions above, the physical state of all of the precursors is a gas. Although not a requirement for CVD, gas phase precursors are preferred because of the ease of which they can be handled in the reactor and metered to control concentration. Like the names of the most common reactions, precursors can be easily categorized according to the chemical group they exploit. Hydrides, halides, and carbonyls are the most traditional precursors. Relatively new to the process of CVD are a new batch of precursors call metal-organic CVD (MOCVD). These precursors use a myriad of complex organic ligands to bind the desired metal ion and transport it to the substrate in the vapor phase. Characteristics common to MOCVD precursors are high vapor pressure and low thermal decomposition temperature⁶. Because of the extreme variability in the organic chemistry associated with these precursors, MOCVD is essentially treated as a separate sub type of CVD with practitioners solely specializing in the use of complex metal –organic precursors. A full treatment of MOCVD is outside of the scope of this writing, but the major talking points of MOCVD will be mentioned. The simplicity of the more traditional precursors naturally tends toward a more comprehensive appreciation and such will be the case here.

Taking into consideration elemental complexity, the first group of traditional precursors is the hydrides. Hydrides are most often used in the electronic industry for the fabrication of semiconductors. Here, hydride compounds are commonly employed to deposit single element such as boron or silicon. Most elements important to CVD process from hydrides, but only a select few are utilized as CVD precursors. Table one, below lists the hydrides most commonly

Element	Name	Formula	Boiling Point (°C)
As	Arsine	AsH ₃	-55
B	Diborane	B ₂ H ₆	-92
Ge	Germane	GeH ₄	-88
N	Ammonia	NH ₃	-33
P	Phosphine	PH ₃	-87
S	Hydrogen Sulfide	H ₂ S	-60
Sb	Stibine	SbH ₃	-17
Se	Hydrogen Selenide	H ₂ Se	3
Si	Silane	SiH ₄	-111
Te	Hydrogen Telluride	H ₂ Te	-2

Table 1-List of Hydrides common to CVD. Reproduced from Handbook of CVD¹⁰

employed as CVD precursors. The primary advantage of hydride chemistry is the cleanliness from thermal decomposition reaction where the only byproduct is hydrogen. A good example of hydride chemistry is the pyrolysis of diborane and phosphine to form boron monophosphide according to the reaction:



The largest disadvantage to hydride is that most of the compounds listed in Table 1 are extremely toxic as well as flammable. Extreme caution must be taken when working with these gases.

Halogens are the second class of precursors commonly employed in CVD. As a group, they are considered reactive and all of the available halogens have been used in reaction chemistry. Halogens are all diatomic gases, an advantage for CVD and can bind to most metals in a variety of different valent states³. The aspects of this have been previously discussed in the reversible transfer and disproportionation reactions. Table 2 lists the halogens and their properties.

Element	Molecular Formula	Electronegativity (KJ g-atom)	Boiling point (°C)	Melting Point (°C)
Fluorine	F ₂	339	-118	-233
Chlorine	Cl ₂	355	-35	-103
Bromine	Br ₂	331	59	-7
Iodine	I ₂	302	184	114

Table 2-List of Halogens used as precursors in CVD. Adapted from Handbook of CVD Pierson¹⁰

Like the hydrides, the halogens are toxic and require caution when working with them. In addition to toxicity, the reactivity of the halogens can prematurely corrode pieces and

components of the reactor system. Material compatibility must be examined prior to the introduction of halogens into the system. Monel and Teflon are examples of materials that can be safely used with halogens¹⁰. Halogens react to form halides. The resultant halides can be gases, liquids or solids at room temperature. Less common than gas precursors, liquid precursors can rather easily be metered in most CVD arrangements. The solid halides however, require heating to place them in the gas phase prior to introduction into the reactions zone of the reactor. The chemistry of metal halides is well established and most of the compounds of interest to the CVD practitioner are commercially available.

The last group of traditional gas precursors is the carbonyls, or more specifically the metal carbonyls. The metal carbonyls are not to be confused with MOCVD. The distinction relates to overall complexity. Metal carbonyls are basic compounds and really consist of just two components: the carbonyl functional group (CO) and a transition metal. Most common are those found in group d of the periodic table¹¹. Some important characteristics of metal carbonyls compounds are that they are hydrophobic and soluble in non-polar solvents such low molecular weight hydrocarbons. Metal carbonyls vary in complexity, with the most simple compound being a mononuclear metal carbonyl with the formula : $M(CO)_x$. More elaborate complexes are common and a few quardrernary metal carbonyls have been identified. Table 3 lists some of the more common metal carbonyls.

Compound	Color and Form	Trait
$Ni(CO)_4$	Clear Liquid	Highly Toxic
$W(CO)_6$	White Crystal	Volatile
$Ir_2(CO)_8$	Yellow Crystal	Sublimes in CO_2 @ 160°C
$Fe(CO)_5$	Yellow Liquid	Volatile
$Fe_2(CO)_9$	Yellow Crystal	Volatile

Table 3-List of Selected mononuclear and dinuclear metal carbonyl complexes. Adapted from Handbook of CVD Pierson¹⁰.

To this point, all of the gaseous precursors discussed to this point have been readily commercially available. Most of the hydride and all of the halogen precursors are available from vendors in sufficient purity that no further filtration is required prior to introduction into the reactor. The metal carbonyls are no exception this, but a two special cases apply where it may prove more practical to synthesize the desired precursor. The compounds in question are nickel $[Ni(CO)_4]$ and iron carbonyl $[Fe(CO)_5]$. In the case of these two compounds the direct reaction of the metal with CO readily produces the desired precursor making this a quick and money saving option for the CVD practitioner^{3,5,10}.

Chemical synthesis is often required for this next of CVD. Metal-organic CVD is relativity new to the CVD scene and only began being widely used in the first half of the twentieth century¹⁰. It is characterized by the desired metal being bound one more carbon atoms of complex organic hydrocarbon group commonly called a ligand. Experiments in the 1960's showed that reactions with these metal organic precursors could be carried out at lower temperature than traditional

methodologies and that the results were epitaxial films—a requirement for the semiconductor industry. It is the combination of these traits that led to broad adoption of MOCVD in the electronic industry. Most of the MOCVD reactions can be carried out well below 1000°C making them attractive for processes with integrated circuits that cannot tolerate elevated temperatures⁸. In terms of process equipment, MOCVD is very similar to a traditional CVD apparatus. The main difference is the ability to heat and meter liquid precursors.

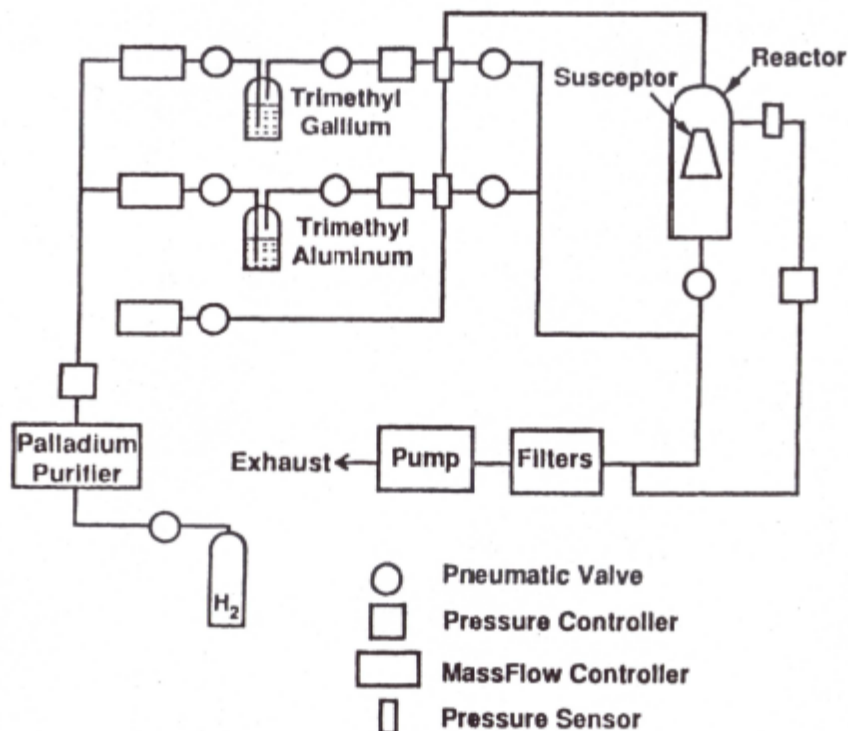


Figure 5-Schematic of generic MOCVD System¹⁰

The high cost of MOCVD precursors and equipment relegate it to processes where the rate on return is high. This means MOCVD is mainly employed in production processes that require high quality is and materials are in high demand such as compound semiconductor applications.

One of the big advantages to MOCVD is the wide selection of precursors available to deposit any number of desired species. Although the term metal is used in MOCVD this can be a misnomer because materials that are not considered metallic such as boron and beryllium are deposited using MOCVD precursors. There are too many to cover in detail, but a significant number of the precursors can be organized according to group. The first major group of MOCVD precursors is the Alkyls. Alkyl ligands are formed from the reaction of aliphatic hydrocarbon or an alkyl halide with a metal¹⁰. A characteristic of alkyl important to CVD is they are generally nonpolar, moderate volatile, a general requirement of CVD and have a low

decomposition temperature. Other major groups of MOCVD precursors include large coordinated ring systems such as alicyclic compounds and aryl compounds. Examples of each are below.

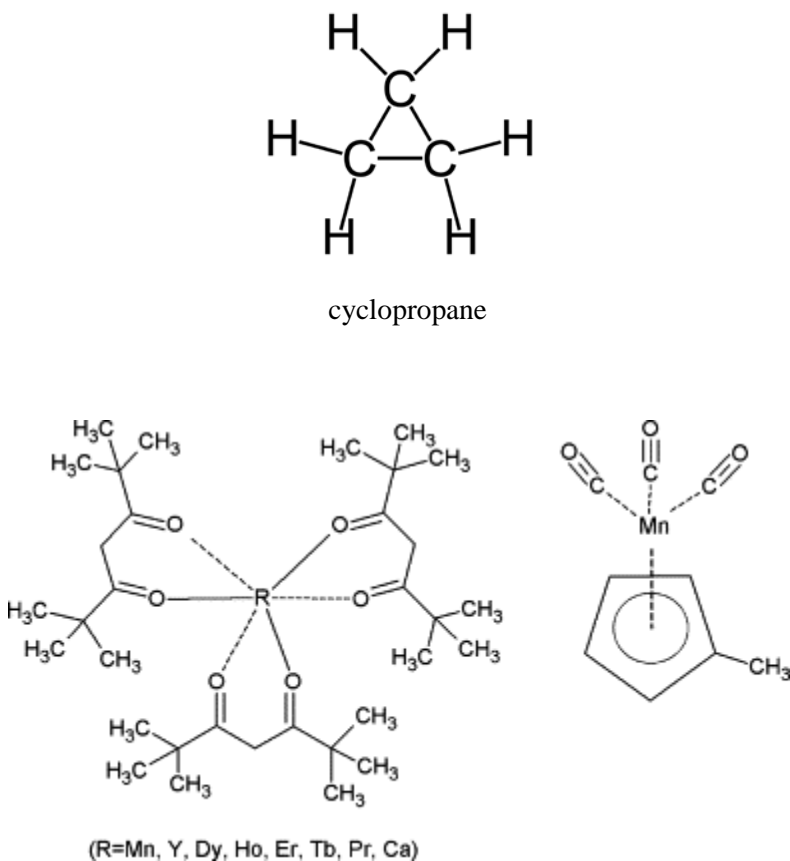


Figure 6-Images depicting examples acyclic (top) and aryl MOCVD precursors

Both acyclic and aryl compounds possess moderate vapor pressures and decomposition temperatures below 500°C.

The last group of MOCVD precursors is the Acetylacetonate compounds. These are more commonly known as metal acetonates and are produced by a reaction between a metal and the ligand acetylacetone. Acetylacetonates, unlike alkyl and alkyoxides are air stable, making

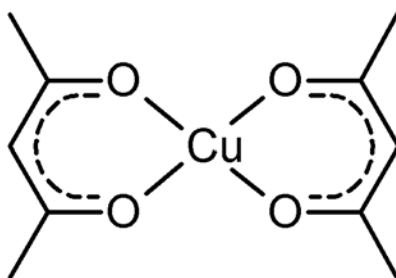


Figure 7-Lewis structure of copper acetylacetonate

handling much easier¹⁰. There is some sacrifice in solubility with these compounds, but all have sufficient volatility to the vapor phase.

The major groups of MOCVD precursors previously described are suitable for the deposition of numerous metal ions. There is a substantial body of work dedicated to specific ligands. By varying the ligand density, specific ligands have been developed for most metals, carbides, nitrides and even oxides. Each has its own specific advantages and disadvantages and unique industry application. MOCVD is still a growing field in CVD and new highly complex precursors are being developed every day. Precursor complexity typically scales with atomic number. Denser metal require larger ligands to achieve the required characteristics for precursors. A commonly employed practice in MOCVD is auto synthesis of precursors. Most of these highly complex compounds are not needed in sufficient quantity to justify large scale production. Therefore, the CVD practitioner will often synthesize precursors prior to deposition. This has led to a boon in metal-organic chemistry and many research groups working in this area conduct dual phase programs into ligand synthesis and MOCVD.

Characterization and Deposition

While transport and chemistry are critical aspects of the CVD process, characterizing the films produced and interpreting the results of the deposition process is equally important. Successful film growth by CVD is not often confirmed until after deposition. Most important film characteristics are not visibly evident by the naked eye. Comprehensive materials characterization often takes a three-pronged approach depending on the specific application. Microscopy in general has become synonymous with materials characterization. The term microscopy here is intended to be all encompassing and include optical as well as the highly touted electron microscope techniques now available. Electron microscopy is a valuable tool for CVD characterization because of the depth of information available in one tool. Modern scanning electron microscopes (SEM) can achieve magnifications of 30,000X, which can allow visualization of particles in a massive 1cm to 50 nm range². SEM's also have a high depth of

field, allowing a wide area to be in focus at one time, and high resolution that allows information rich areas to be magnified.

Generally speaking, scanning electron microscopy works by rastering the surface of interest with a beam of high energy electrons. The beam originates from a source called a gun and passes through a set of optics and coils designed to condense and focus the beam on the sample².

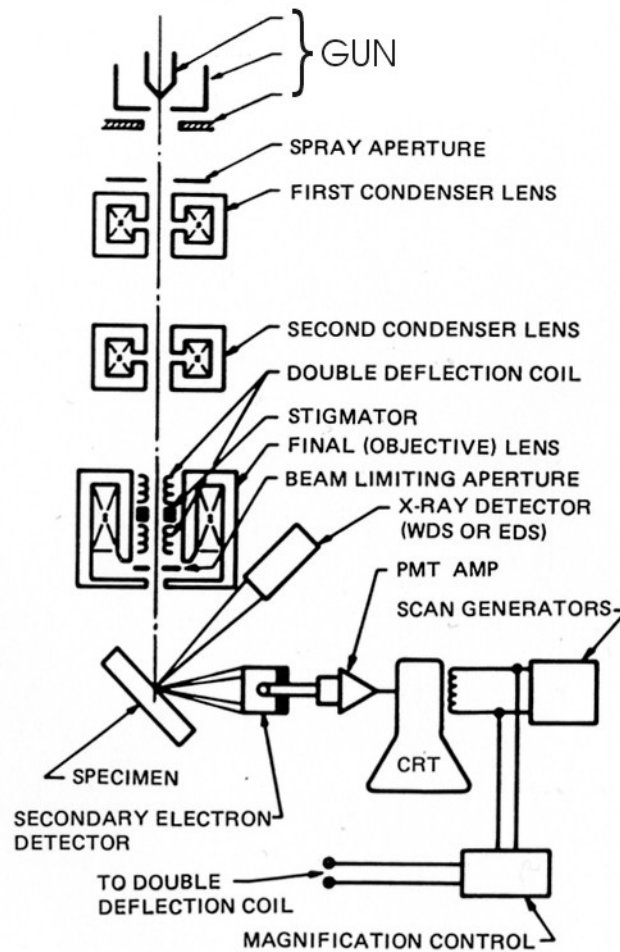


Figure 8-Schematic of SEM¹⁴

Once the electron beam impinges on the sample surface, a number of interactions take place that can be detected and an image produced. While high-energy electrons can pass through thin samples with little or no interaction, SEM analysis relies on the elastic or inelastically scattered electrons and radiation produced by inelastic scattering to produce the desired information.

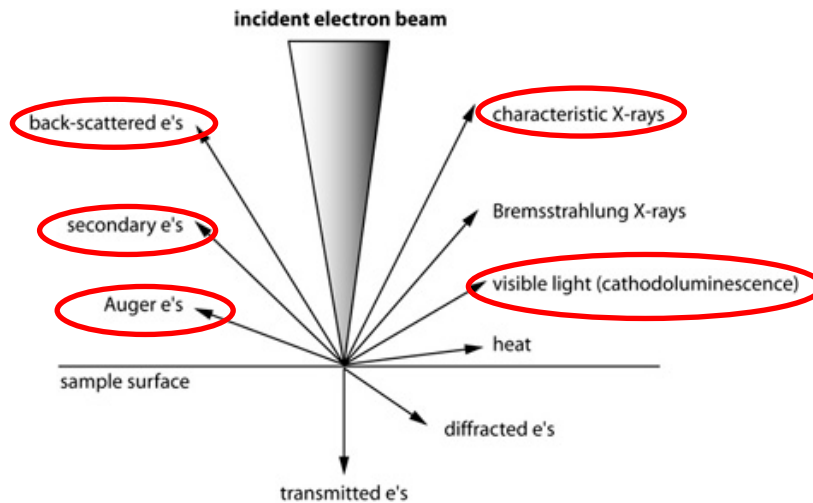


Figure 9-Diagram of possible electron interaction from SEM probing¹⁴

The interactions typically used in image creation are circled in red. Bremsstrahlung X-rays are not specific but form an energy continuum from very low energy to the energy of the incident beam. This creates a characteristic background radiation that can mask some of the characteristic X-rays. The beam quality is dependent on the energy of the incident beam, the interaction volume in the sample and the orientation of the volume with respect to the incident beam. Asymmetry in the interaction volume will produce an askew image. To produce an image, each of the aforementioned interactions are detected independently and have specific resolution with Auger and secondary electrons producing the highest resolution followed by backscattered electrons, cathodoluminescence, and lastly Bremsstrahlung².

Aspects of Transmission Electron Microscopy (TEM) and Scanning Transmission Electron Microscopy (STEM) are similar, but these also have distinct differences that provide advantages in materials investigation. Like SEM, TEM and STEM use a high-energy electron beam and a series of focusing electron optics to place the beam on the sample. The key difference from SEM is that TEM and STEM do not rely on a series of scattering interactions to produce an image. In lieu of scattered electrons, TEM and STEM rely on electrons transmitted through the sample for imaging. This reliance on transmission electrons brings with it a series of rigorous sample preparation requirements that are often difficult to perform and time consuming. The payoff for the difficult sample preparation can be large, in that TEM and STEM offer tens of millions X magnification and down to 0.5 angstroms resolution. This magnification and resolution provide the ability to observe fine crystal structures and material interfaces.

In addition to providing high magnification of sample surfaces (SEM) and bulk morphology (STEM, TEM), each instrument typically has additional analytical capabilities based on the inherent electron interactions. Common to most SEM's is an Energy-Dispersive X-ray (EDS) or Electron Backscatter Diffraction Analysis (EBSD). EDS analyzers are more common than EBSD and use the characteristic X-rays emitted from the bombardment of the compositional elements

of the sample from the electron beam. Light elements below atomic number 4 cannot be detected using EDS.

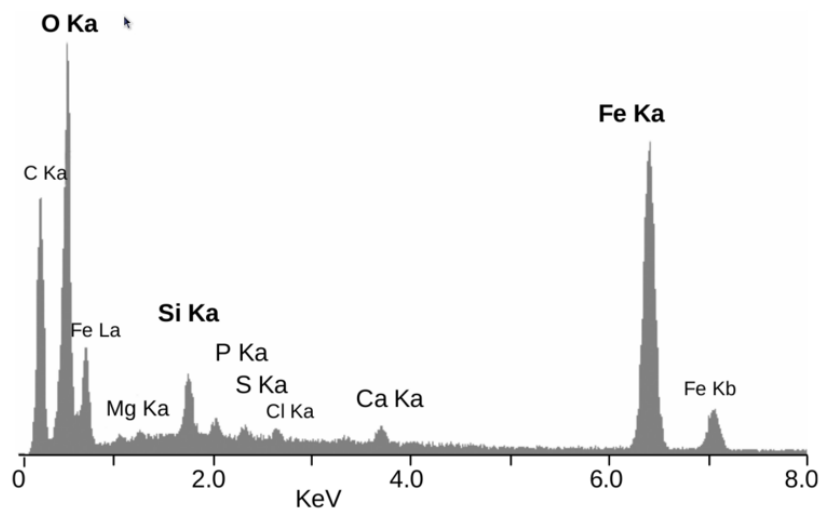


Figure 10-Example EDS Spectrum showing elemental peaks

Unlike EDS which is a compositional analysis tool, EBSD is a morphological tool designed to show crystallographic orientation of the surface of the sample being probed. It works by the principal of fluorescence. A prepared sample is placed in the SEM chamber at a high angle. The sample is then juxtaposed to a phosphor screen already in the chamber and part of the EBSD detector system. The sample is then irradiated with the high energy electron beam. The backscattered electrons that exit the sample at the Bragg condition are detected by the phosphor and fluoresce. The resultant image is the backscatter diffraction pattern that can be further processed with the Miller indices of the diffracting plane to form the surface crystallographic orientation.

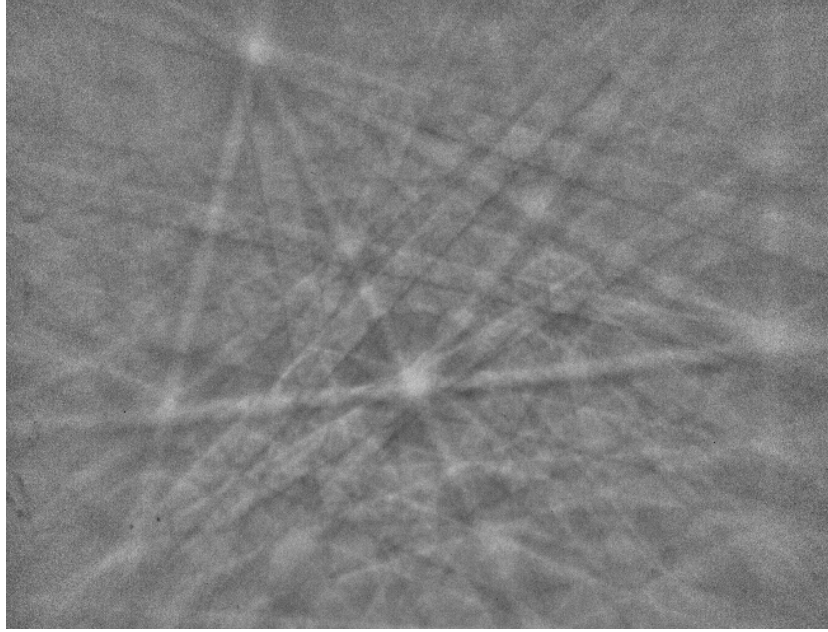


Figure 11-EBSP pattern of quartz

Another material characterization tool associated with TEM is electron energy loss spectroscopy (EELS). EELS is a valuable technique for bulk compositional analysis. The inherent problem with compositional analysis tools on electron microscopes is sensitivity. EDS and EELS are generally limited to the percent level in terms of elemental composition. This is fine for a number of causal material investigations, but semiconductor device manufacturers are often concerned with dopant or contaminations in much lower elemental concentration. Silicon wafers are often doped with boron or phosphorous to create P-type or N-type semiconductors and to tailor the resistivity of the wafer. Typical dopant levels are sub ppm, which are far out of the range of compositional X-ray and high level electron interaction techniques. Two techniques are considered the standard in high sensitivity for elemental composition. They are secondary ion mass spectrometry (SIMS) and Auger electron spectroscopy (AES). SIMS is a mass spectrometry based technique where an ion (Ar^+ , Cs^+ , O^-) beam is rastered over the surface of a sample. As a result of the interaction between the ion beam and the sample, secondary ions from the sample surface and near surface region are ejected from the sample matrix. These ejected species are transported to the mass analyzer where their mass to charge ratio is ascertained. SIMS is not limited in the elements it can detect and magnetic sector instruments can resolve individual isotopes from hydrogen to uranium. Detection limits for SIMS is in the sub ppb range, making it an excellent choice for trace detection and dopant quantification. The downside to SIMS is the incident particle beam tends to be destructive to the sample if power levels are not closely examined. Availability can be a concern as well with typical cost of a SIMS now exceeding \$1M².

Another viable compositional method for material characterizations is Auger Electron spectroscopy (AES). Similar to the tools associated with electron microscopes, AES uses an electron beam to impinge on the surface of the sample. The key difference in Auger and EDS is the detected species. AES detects the emitted Auger electron and not an X-Ray. Advantages to AES compared with EDS are significant and include high surface specificity, probing depths between 5 and 100Å, high lateral spatial resolution compared to EDS which can approach 300Å. Most importantly, the detection level for AES is in the ppm range. Like EDS, AES cannot detect hydrogen or helium. The Auger process works by the production of an inner atomic shell vacancy created by the primary electron beam. This vacancy, typically created in the K shell, is filled by an electron from an outer shell which is accompanied by release of excess energy by emission of a valence electron. The electron transitions and the binding energy give way to an elemental specific electron energy emission. Application of AES sensitivity factors allows quantitative AES to be performed.

Although electron microscopy and compositional techniques do not encompass all of the applicable approaches for material characterization, they do provide key information on morphology, structure and composition. The third prong in comprehensive characterization is electrical property measurement. These techniques are more application driven since not all material investigations necessitate the probing of the electrical properties. The coatings industry is a good example of this, vacuum coaters seldom care about the ability of tool wear coatings to conduct a signal. Therefore, electrical property characterization is more specific to the semiconductor industry for eventual device fabrication. Since electrical property measurements are more of a niche they will not be explained in detail. Techniques can vary widely in complexity and required equipment. One of the most basic electrical parameters to measure is sheet resistivity. More applicable to thin film samples, a known current and voltage is applied to the surface of a sample and resistance is calculated from the plot of current vs. voltage. More involved measurements involve photoluminescence spectroscopy which can probe the band gap of a material, identify impurity levels and even locate certain kinds of growth defects. Lastly, Hall effects measurement can be employed to determine the charge carrier concentration and hole mobility. This powerful technique is applicable to conductors and semiconductors. It uses the application of magnetic fields and current with respect to the applied field to determine the distribution of electron flow in the sample.

The objective of chemical vapor deposition is to ultimately establish a link between system growth parameters and sample composition, morphology, and electrical properties. The method to establish this correlation is experiment. Samples are grown with documented parameters (pressure, flow, temperature, etc...) and then characterized using some or all of the methods described above. Repetition is necessary to establish a cause and effect relationship. There can be many subtleties to how process parameters can affect the outcome. Small variations in temperature, perturbation in flow from a slight variation in surface roughness can affect deposition quality. That is why industries that rely on CVD spend millions of dollars engineering

out as many process variations as possible. This is often not possible on smaller lower throughput systems. Despite these conditions, there does exist a set of common objectives that all CVD practitioners aspire to: high quality. Quality by its very nature is hard to quantify. Many have attempted through countless experiments tried to establish criteria for what is considered high quality. The problem with this methodology, is quality is highly relative. Intended application of the material tends to dominate arguments on product quality. Some might consider amorphous material suitable for their needs while others consider it total failure.

One example of this is epitaxy. There are two main types of epitaxy: homo and hetero. Homoepitaxy takes place when the deposited material and the substrate match. An example of this would be deposition of Si on Si wafers. In contrast, heteroeptitaxy occurs when the

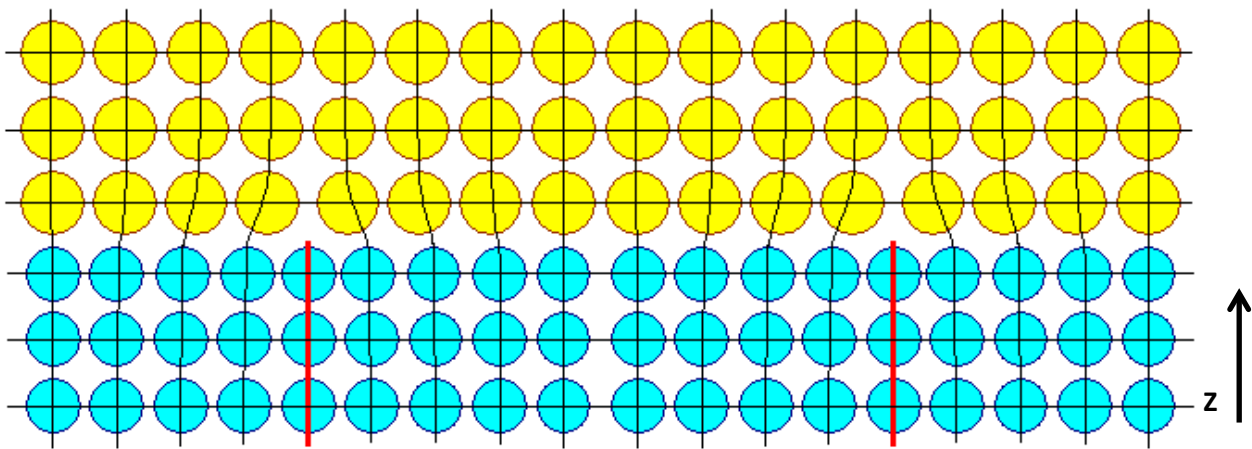


Figure 12-Simplified diagram showing heteroepitaxy. Note the direct relationship between the positions of the atoms in the yellow deposited layer and the blue substrate¹⁵

deposited material and the substrate differ. Heteroepitaxy is somewhat more challenging in that maintaining high quality epitaxy in differing materials is not straightforward, Inherent barriers exist and include induces strain, defect creation, stacking faults, etc.. Some of these problems exist in homoepitaxy, but not often to the degree in heteroepitaxy. One strategy to minimize defects in heteroepitaxy is to employ lattice mismatch minimization. This process involves selecting materials for CVD that have similar crystal lattice structures. This is not always possible, based on application, but the more similar the materials, the less likely growth defects will proliferate. A convenient way to express relationships in lattice mismatch minimization is to report percent lattice mismatch between the materials. Percent lattice mismatch is related to the mismatch strain and is based on the room temperature material specific lattice constants and can be easily determined from the following formula¹.

$$f \equiv \frac{a_s - a_e}{a_e}$$

Where a_s and a_e are the relaxed (room temperature) lattice constants of the substrate and epitaxial layer respectively. Typical values for practical lattice mismatches are below 10%. In some unique circumstances epitaxy can be achieved with values up to 14% and higher. However, these instances are exceedingly rare and success is usually based some specific material behavior.

There are numerous defects common to materials deposited by CVD and detailed treatment will not be addressed here. Basically, there are three types of defect common to solids: Point defects, line defects and surface imperfections. Point defects are localized imperfections and are often formed when an atom is missing (vacancy) or is out of place in the crystal lattice⁷. The connotation of out of place atoms is broad enough to incorporate extra atoms as well. Interstitial impurities are also considered point defects in solids. Figure 13 shows the most frequently observed point defect in solids.

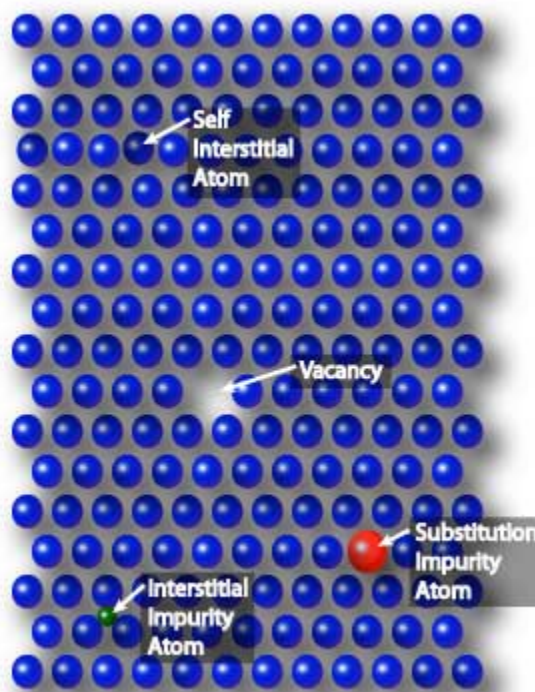


Figure 13- Diagram showing examples of common point defects in solids¹⁵

Line defects in solids by definition more pervasive in deposited solids and extend along one line of atoms in the lattice. The most common type of linear defect is the dislocation. The term dislocation refers to the scenario when atoms are out of place in the lattice, thus causing a distortion of the lattice. Stress induction during growth is responsible for most dislocations. The two subtypes of dislocation are edge and screw⁷. Edge dislocations are gross defects that are easy to observe. They exist as an extra half plane of atoms in the lattice. Figure 14 depicts an edge dislocation

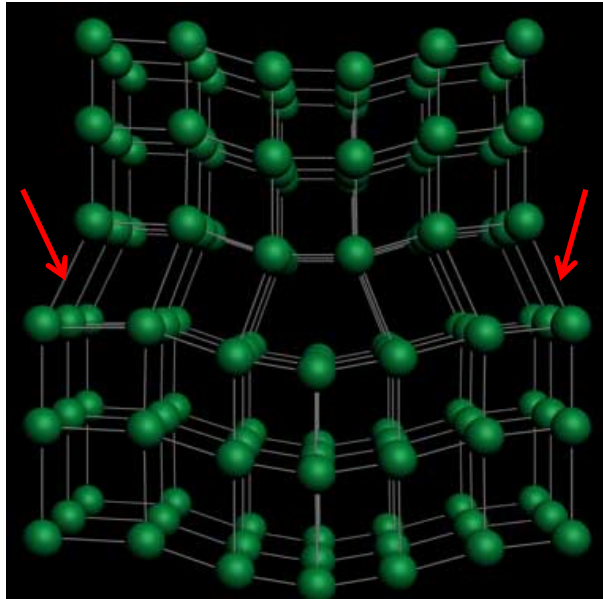


Figure 14-Diagram of edge dislocation solid. The red arrows pointing to the extra row and resultant lattice distortion ¹⁵

Unlike line edge dislocations which propagate parallel to the defect, screw dislocations form perpendicular to the location of the stress in the film. They are typically associated with the presence of shear stress in the film and are for this reason more difficult to observe⁷.

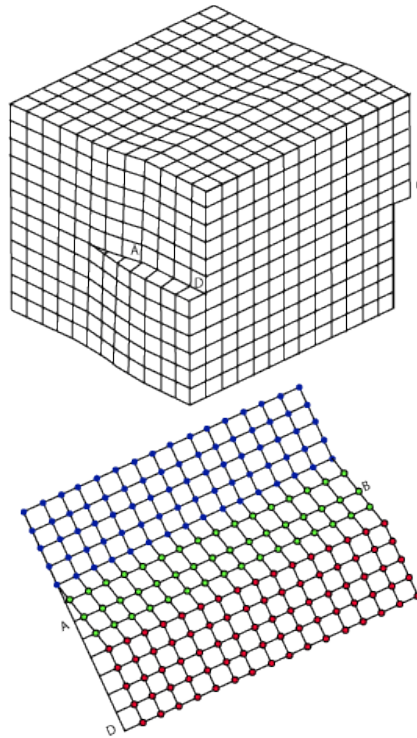


Figure 15-Image of screw dislocation. The blue lattice depicts atoms in their correct orientation. The red atoms are those that have been shifted to a new location within the lattice. The green atoms are in the process of shifting¹⁵

Line defects that extend to additional planes are called planar defects. The most common cases of planar defects are stacking faults and twin boundaries⁴. Stacking faults occur when there is a disruption of the stacking sequence in the atomic planes. See below for an example of a stacking fault in a hexagonal system.

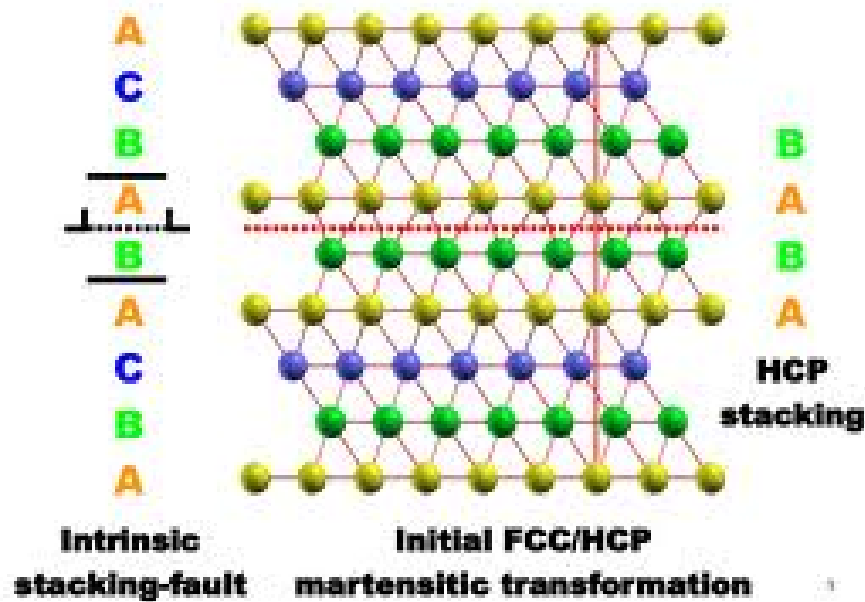


Figure 16-Diagram of intrinsic stacking fault in a hexagonal closed pack lattice

The last planar defect worth discussing is twin boundary formation. Twin boundary defects possess a key difference in comparison to the previously discussed defects. Twin boundary formation occurs at the junction of two basic crystal units rather forming entirely in one crystal like the aforementioned line and point defects⁶. Solids are generally formed from the interconnection of crystals called grains. The point in space where these crystals unite is referred to as a grain boundary. Grains are typically characterized by size and can range from nanometers to millimeters in magnitude. Research into metallurgy has established a link between grain boundary size and cooling rate. Rapid cooling is associated with smaller grains where slow cooling creates larger grains¹². Grain boundary implication on materials is highly application dependent; however, grain surface area within a layer correlates to higher strength.

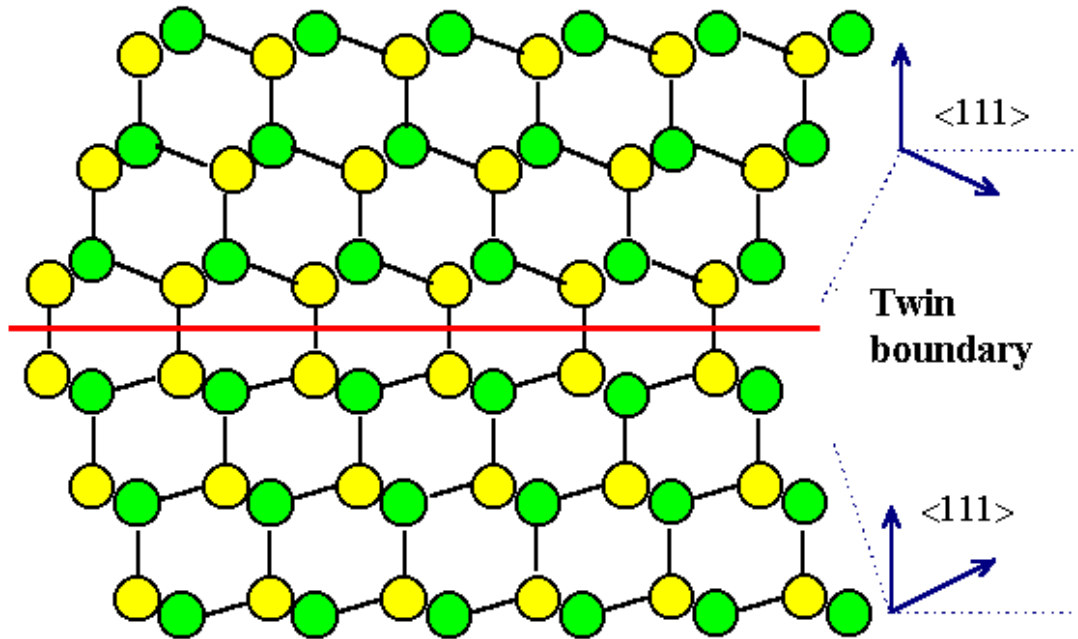


Figure 17-Image of twin boundary formation in the $\langle 111 \rangle$ plane²⁰

Surface defects incorporate the final group of defects in solids. As their name implies they exist solely on the outer surface of the solid and are not necessarily directly related to the point and line defects discussed prior. Undoubtedly however, if a point or line defect was to form near the surface of a solid, it would have some visible impact on surface orientation. A common attribute to a surface defect will be an unsatisfied or dangling bond. The increase in free electrons can readily form hydrides and oxides and induce line and point defects on the crystalline surface.

In order to understand how defects form in solids, it is necessary to relate the growth process to gross structure formation. As a result of this, there are a group of structure growth modes that can help explain the origin of crystal and bulk morphology. In CVD processes, resultant structure formation begins in the gas phase, not in the solid as commonly thought. Particle nucleation of the gas whether on or above the substrate is the fundamental precursor to structure formation. Nucleation is the term used to describe the process from which the gas transforms into a solid. Thermodynamically, nucleation results in an overall reduction of ΔG for the system⁸. This is an important aspect to note in that recalling the discussion on modeling CVD, ΔG minimization is the primary tool used to predict product formation. The direct correlation to solid-gas formation adds validity to the model. In order to better describe the concept of nucleation, it is helpful to introduce the idea of surface energy⁹. Surface energy is created from intermolecular attraction from reduced proximity in the solid phase. The surface energy, γ in solids is dependent on an entropy factor, which in turn, relates to the overall surface disorder of the surface. During the growth process, both the surface energy and the entropy factor are in flux. Structure formation

proceeds because the ordered arrangement of the atoms of a solid phase minimizes the Gibbs free energy in that respecting phase¹². The magnitude of the Gibbs free energy varies with different crystal structures. Some of the most stable are body-centered cubic (bcc) face-centered cubic (fcc) and hexagonal closed pack (hcp). In ideal conditions, the now nucleated solid particles from the gas phase impinge on the surface and spread out evenly because this is the most energetically favorable condition. This layer –by-layer growth is called Frank-van der Merwe growth and is coveted in thin films because it typically gives rise to the most ordered arrangements^{9,12}. Layered growth is achieved by a balance in the bonding between the film and substrate. Another growth mechanism where film and substrate bonding is insufficient and three-dimensional islands are formed. This is referred to as Volmer-Weber growth. A hybrid case does exist when an initial monolayer is deposited on the substrate and then the growth mode changes to form islands. This is called Stranski-Krastanov growth^{9,12}.

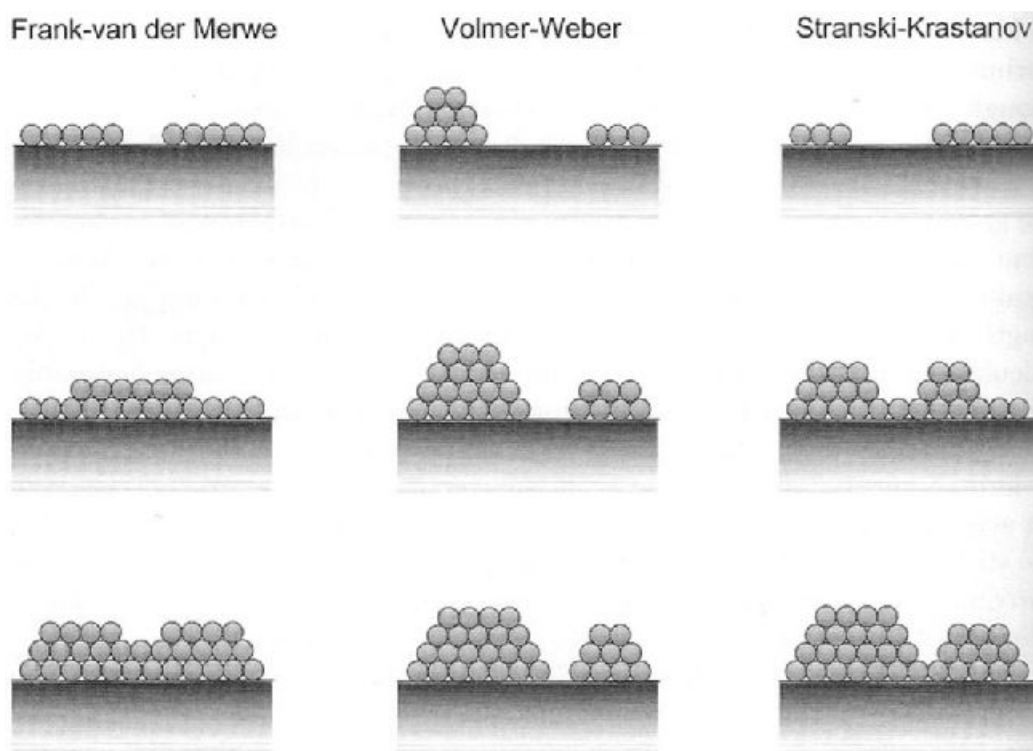


Figure 18-Ball and stick model of three common growth modes¹⁹

In terms of desirability, layered growth is the most coveted because is generally associated with the least propagation of defects. The two island growth modes are less desired because of the increased tendency to form grains at the junction of the islands. With that said, preferred growth modes, like many other aspects of CVD is application specific and the individual advantages and disadvantages must be thoroughly considered to maximize success.

Conclusion

Chemical vapor deposition, by its very nature, is a complex blend of several disciplines. Concepts more thoroughly discussed in the fields of physics, chemistry and materials science are required to adequately understand CVD. The intention of this manuscript was to briefly summarize the essential concepts related to success in CVD. The layout of content in this work is designed to treat subjects in order s in relation to the phase of the CVD project. Topics of fluid flow, heat flow and modeling are typically entertained during the very early phases of a project. Notions of process chemistry encompass both the early stages and construction phase of a reactor for a set of CVD experiments. Characterization and deposition were covered last because they are important only in post deposition. Despite being heavy in theory which can be considered at any point in the process, deposition modes are only evident after some sort of material characterization has been performed. There is an abundance of resources for less concise treatments of the subject. They include texts solely focused on CVD and texts direct at more specific topics such crystal defects, fluid dynamics and electron microscopy. All of the mentioned above was employed in the creation of this manuscript. The author would like to acknowledge the contribution of Professors Chuck Feigerle and Phillip Rack for their support and encouragement throughout the process.

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