

orientation. This process, known as epitaxy, plays a major important role in solid-state technology. **7. Impurities:** Since CVD only uses high-purity gases, the amount of contaminants that could be incorporated to the film is greatly reduced. **8. Flexibility.** By simply varying the deposition conditions or the precursors ratio, both chemical composition and physical properties can be tailored during its growth. Thence, it permits to obtain well-defined multi-layer structures with controlled impurities and stoichiometries. **9. Adaptability.** CVD processes can be easily adapted from research level to mass production.

But CVD also has some drawbacks. Some of them are caused by its own advantages and others are due to the working principles. The most significant example of the first case is the system complexity and the high number of variables that needs to be controlled. Moreover, depending on the working conditions, it could be possible to obtain materials with opposite properties using the same precursors. Although it clearly is an advantage, if it is not properly controlled, it also is its main drawback. The inherent CVD problems are due to the gases used, both precursors and carriers. If the reaction is not completely heterogeneous and/or all reaction sub-products are completely desorbed, they would be incorporated into the growing film, causing its contamination.

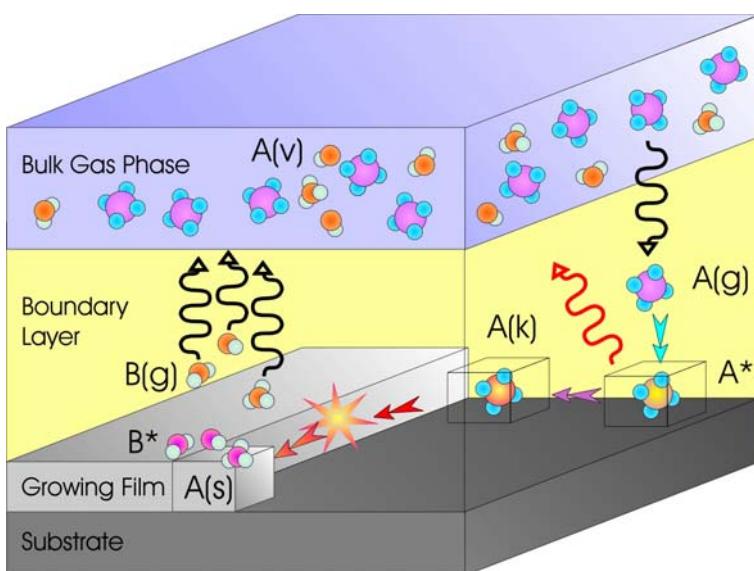


Fig. 3.2: Standard model employed for the growth mechanism in CVD processes.



The growth in a CVD process can be explained with the help of fig.3.2. It has the following reactions sequence:

- The precursors molecules A(v), diffuse, due to a concentration gradient, from its initial position at the bulk gas zone, through the boundary layer (the thickness of which depends on the working conditions), reaching the grown surface A(g).
- Once the precursor reaches the substrate surface, it is adsorbed A* and diffuses at substrate level until it is desorbed or until it finds a position were it can form a tighter bond (i.e., a crystallographic step), A(k)
- The precursor keeps on diffusing along the step until it finds an stable nucleation point. Then, a chemical reaction is produced, providing the stable nucleus to the growing layer A(s). The residual reaction products B* diffuse along the film until they are finally desorbed B(g) and then diffuse across the boundary layer until they reach the bulk gas phase.

Using CVD technique, it is possible to obtain amorphous, poly-crystalline and mono-crystalline films. The crystallographic state of the deposited layer will depend on the material itself, but also on the working conditions, as could be temperature, diffusion length and growth rate. Concerning the growth rate, it would be extremely useful determining what factors are the limiting step in CVD reactions, that is, what controls the overall deposition process. Obviously, if it is known, it would allow to optimize the deposition conditions, enhancing the deposition rate and, to a certain extent, control the layer properties.

According to the previously described CVD deposition scheme, the deposition rate (G) depends on the mass transport from the bulk gas zone to the substrate surface and the rate at which they react once they have reached the surface, following the relation [10]:

$$G = \frac{A}{\frac{1}{F} + \frac{1}{R}} \quad (3.1)$$

where A is a constant that depends on the geometry of the reactor, while R and F stands for the surface reaction and the mass transfer rate, respectively.



At a given temperature, the surface reaction rate is

$$R = k_1 C_s \quad (3.2)$$

where k_1 is the chemical reaction constant and C_s is the concentration of the reactant at the substrate surface which, in turn, is proportional to the partial pressure of the gas. Since reactant partial pressures generally are similar in processes at different pressures, the surface reaction rate does not have sharp variations. This is not so in the mass transfer rate, which reads

$$F = \left(\frac{\Lambda}{\delta} \right) \Delta C \quad (3.3)$$

where Λ is the gaseous diffusivity, δ is the boundary layer thickness and ΔC stands for the reactant gas concentration gradient between the substrate and the bulk gas flow. The diffusivity is known to be inversely proportional to the total pressure (i.e. $\Lambda = k_2/P$, where k_2 is a constant) while the boundary layer is proportional to the *Reynolds number* and can be written as

$$\delta(z) = \sqrt{\frac{z}{R_e}} = \sqrt{\frac{z\eta}{\rho U}} \quad (3.4)$$

in which ρ is the gas density, η is its viscosity and U stands for the gas flow velocity. If perfect gases are considered, then eq (3.4) can be rewritten as

$$\delta(z) = \sqrt{\frac{RT\eta}{M}} \sqrt{\frac{z}{PU}} \quad (3.5)$$

where M is the molar mass of the gas, T is the temperature and R is the gas constant.

In the case of control by surface reaction kinetics, the growth rate is dependent on the amount of reactant gases available. As an example, suppose a CVD reactor working at low temperature and pressure values. The low pressure causes its diffusivity through the boundary layer to be very high. If pressure is decreased by three orders of magnitude, diffusivity is increased by a factor of 10^3 and δ is 3 to 10 times larger than in the processes done at high pressures. Thence, the value of F is increased more than 10^2 , while R is kept nearly constant. In the final deposition rate, the term containing the mass transport becomes small and ineffective, and the deposition rate only depends on the surface reaction. The low temperature causes the reaction to occur slow since there is



little energy to enhance the reaction, then, there is an excess of reactants at the surface and its reaction is the limiting step in the film growth.

On the contrary, processes done at high pressure and high temperature are diffusion-controlled. As a result of a high pressure, the gas diffusivity is low and both terms in eq (3.1) become comparable in magnitude. High temperature does not cause a diffusion enhancement, but a surface activation, causing that any precursor molecule that reaches its surface reacts instantly. Thus the bottleneck factor in this situation is the in-diffusion coefficient of the precursors through the boundary layer and the out-diffusion of the residual reaction products.

Thence, since normally the surface kinetics is the limiting step at lower temperatures and at high temperatures processes are diffusion-controlled, it is possible to switch between both deposition mechanisms simply by varying the deposition temperature. As an example, an Arrhenius plot using several precursors lead to the deposition of silicon is shown in fig. 3.3. In the A sector, the deposition is controlled by surface reaction kinetics, while in B zone, the deposition is controlled by diffusion. The growth rate is linearly related to the precursor partial pressure. It also can be seen that the transition between both mechanisms is not abrupt, thus, there exists a zone where both processes are significant.

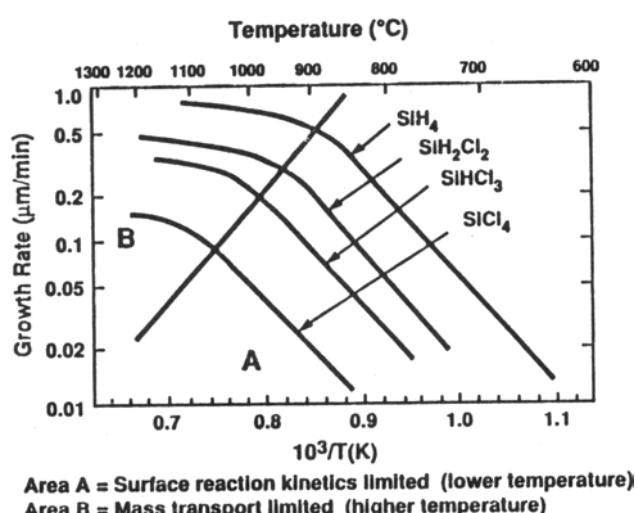
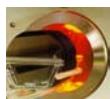


Fig. 3.3: Arrhenius plot for silicon deposition using various precursors [11].



There exists several CVD classifications according to the total pressure (High Pressure/Low Pressure), the kind of precursors (Metal-Organic) and the method of energy transfer (Resistance/ RF heating/ Plasma Enhanced/ UV Excitation/Laser Excitation). Moreover, what is commonly done is to combine several of the above mentioned techniques so as to take benefit from their advantages, as could be Plasma Enhanced CVD at Low Pressure. Among all the different configurations, we will analyze APCVD (atmospheric Pressure CVD), LPCVD (Low Pressure CVD) and PECVD (Plasma Enhanced CVD) since they are the most commonly used for layer deposition in integrated optics technology.

Atmospheric and Low Pressure CVD

As it was shown before, systems working at atmospheric pressure generally work under the mass-transport regime. Then, the reactor configuration and the wafer stacking are, for a given process conditions, the main responsible of the quality of the layers obtained. Some of its properties are summarized in table 3.3.

When the limiting factors were studied, it was observed that the effect of the pressure on the deposited layer properties was extremely important, since it was the responsible (as it also was the temperature) of working at different regimes. Although APCVD systems have a high deposition rate, they are susceptible to have gas phase reactions, causing a layer contamination. Moreover, due to this high rate, the uniformity, density and step coverage are generally poor. Some precursors in AP reactors must be highly diluted in order to prevent gas-phase nucleation, but it also causes the growth rate reduction. Nevertheless, atmospheric reactors are cheaper, simpler and can operate faster, on a continuous basis. They are primarily used for epitaxial growth of silicon films and binary and ternary compounds, as could be GaAs, InP or AlGaAs. They are also used for depositing, at high rates, SiO₂ or Low Temperature Oxide (LTO) when the layer requirements are not strict (mainly acting as passivation layers).



APCVD (Atmospheric Pressure)					
Temp. (°C)	Reactor properties	Working regime	Advantages	Disadvantages	Materials
600-1000	Hot wall: Deposition everywhere. Periodic cleaning. Cold Wall: Local deposition.	Diffusion controlled (mainly)	Simple. High deposition rate (>1.0 $\mu\text{m}/\text{min}$)	Poor step coverage. Particle contamination. Poor uniformity.	Si SiO_2 Si_3N_4 GaAs InP LTO
300-450					

Table 3.3: Standard configuration and general properties of an APCVD system.

The basic LPCVD system structure is shown in table 3.4. As previously mentioned, at low pressures, the effect of diffusion is far less critical than at high pressure. In practical terms, it means that LP systems, as compared to atmospheric pressure reactors, provide films with more uniformity, better step coverage and improved quality. The better film uniformity is thanks to the low pressure, which substantially increases the precursors diffusivity. The reason that a large number of wafers can be simultaneously coated is due to the fact that, at low pressures, the growth rate of the film does not depend on the flow conditions of the gas (i.e. the mass transfer), but only of its temperature (or pressure) that controls the surface reaction. Another advantage is that while some reactants in atmospheric pressure reactors must be highly diluted to prevent vapor phase precipitation, this is not necessary at low pressure. Therefore, growth rates are lower as compared to AP reactors. However, it is widely used in the highly competitive semiconductor industry due to the high density of



substrates that can be processed in one batch. It is mainly used for depositing layers of insulators (SiO_2 , Si_3N_4), amorphous and polycrystalline silicon, refractory metals and several other elements and compounds.

LPCVD (Low Pressure)						
Temp. (°C)	Press. (Pa)	Reactor properties	Working regime	Advantages	Disadvantages	Materials
600-1000	<100	Hot wall: Deposition everywhere: Periodic cleaning	Surface reaction controlled (mainly)	Excellent purity and uniformity. Good step coverage. Large wafer capacity.	High temperature Low deposition rate	Si SiO_2 Si_3N_4 Doped LTO Undoped LTO Polysilicon W WSi_2

Table 3.4: Standard configuration and general properties of a LPCVD system.

Reactors used in AP- and LPCVD can be either hot wall or cold wall. This term states the temperature that have the reactor's walls. A hot wall reactor is essentially an isothermal furnace which is generally heated by resistance elements. The wafers are loaded, vertically or horizontally stacked. Then, the temperature furnace is raised until the working temperature and the precursor gases are introduced inside the reactor controlling its pressure. The main advantage of hot wall reactors are the very accurate temperature control, that can be up to $\pm 0.5^\circ\text{C}$. The major drawback for this reactor is that deposition is not only done on the wafers, but everywhere, including the reactor