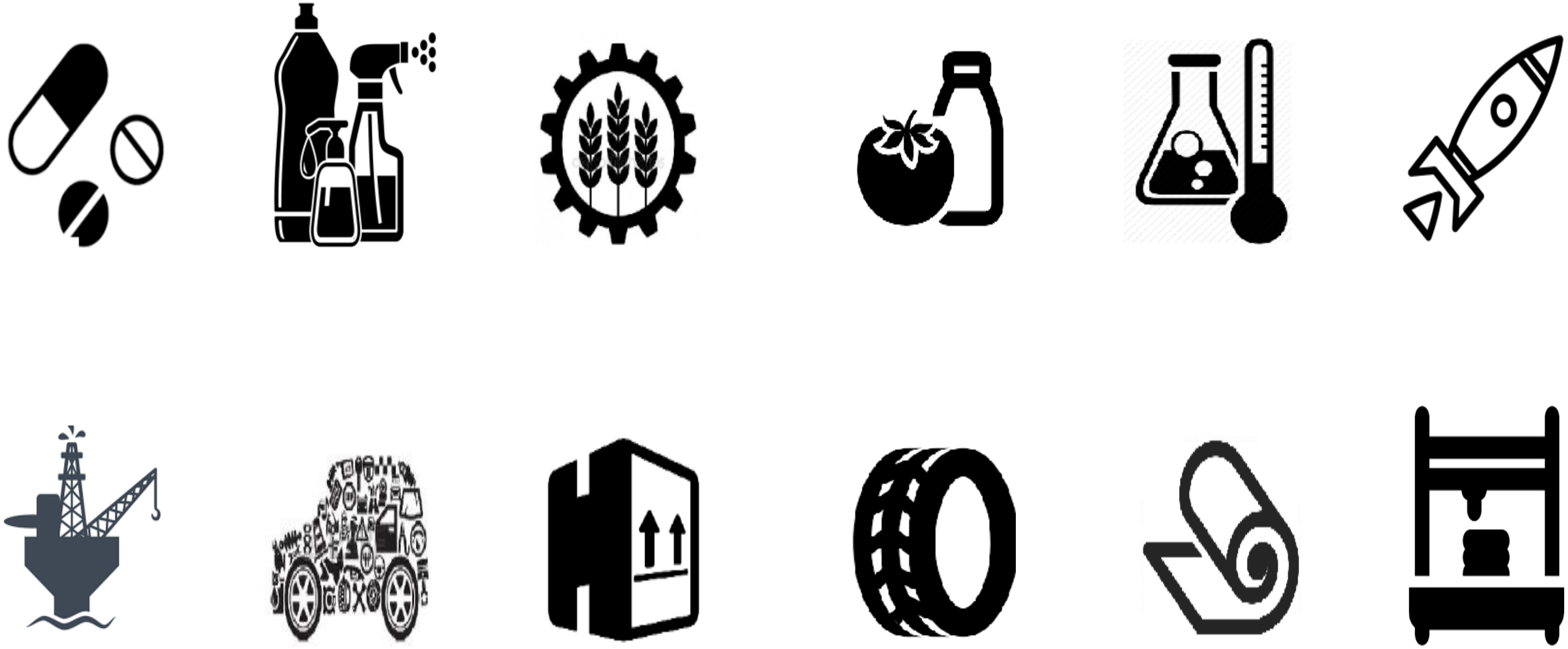

KERONE

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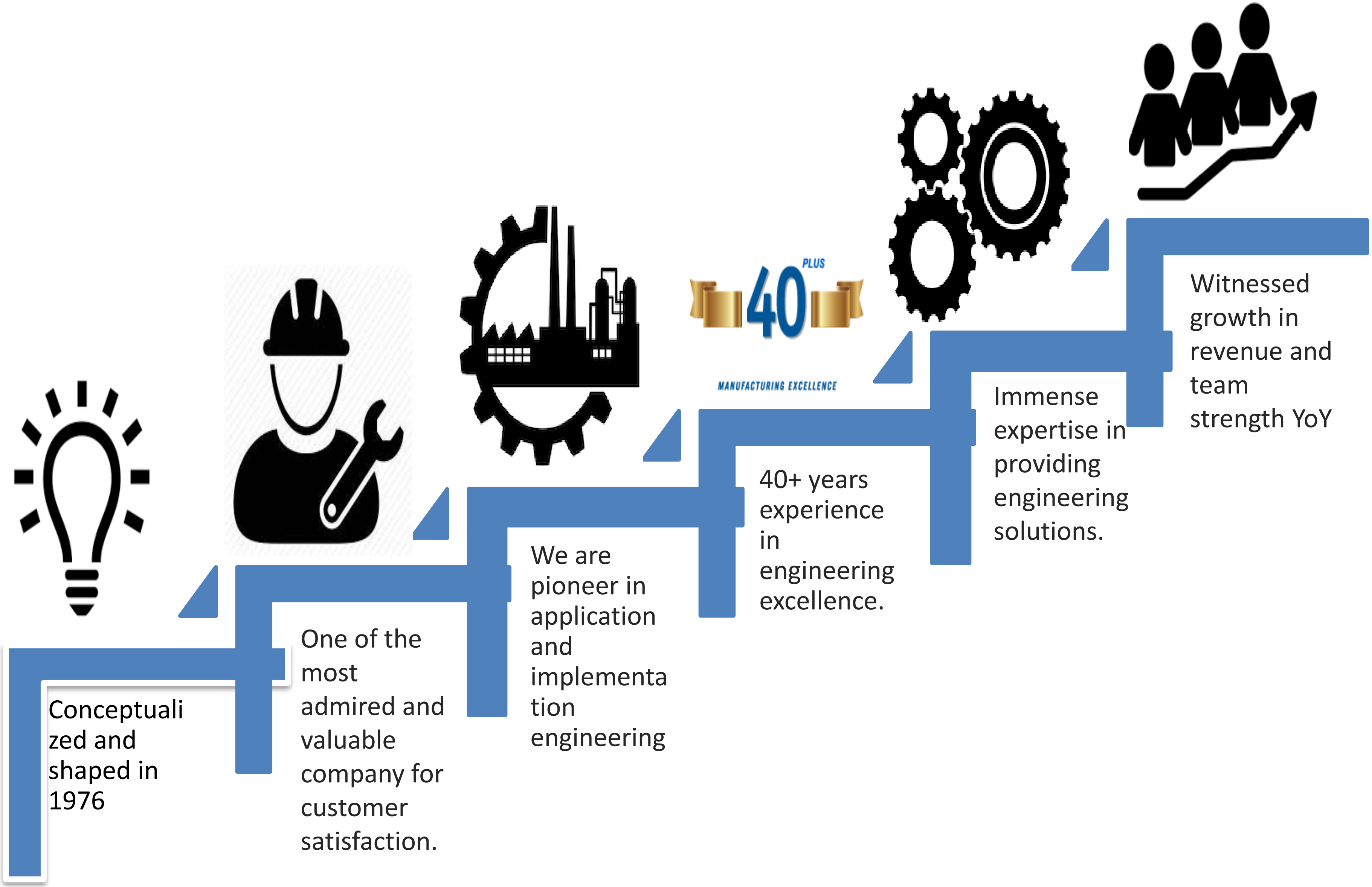

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Introduction:

- Chemical vapor deposition may be defined as the deposition of a solid on a heated surface from a chemical reaction in the vapor phase. It belongs to the class of vapor-transfer processes which is atomistic in nature that is the deposition species are atoms or molecules or a combination of these. Besides CVD, they include various physical-vapor deposition processes (PVD) such as evaporation, sputtering, molecular beam epitaxy and ion plating. In its simple incarnation, CVD involves flowing a precursor gas or gases into a chamber containing one or more heated objects to be coated. Chemical reaction occur on and near the hot surfaces, resulting in the deposition of a thin film on the surface. This is accompanied by the production of chemical by-products that are exhausted out of the chamber along with unreacted precursor gases. As would be expected with the large variety of materials deposited and the wide range of applications, there are many variants of CVD. It is done in hot wall reactor and cold wall reactors, at sub-torr total pressores to above atmospheric pressures, with and without carrier gases, and at temperature typically ranging from 200-1600 o c. There are also a variety of CVD processes, which involve the use of plasmas, ions, photons, lasers, hot filaments, or combustion reactions to increase depositon rates and/or lower deposition temperatures.

CVD Reactor Types

Hot wall reactor is a high temperature chamber in which the substrate is placed for coating. In this including the substrate, all other parts (inlet and outlet tubes) inside the chamber get coated.

A schematic for a hot-wall reactor that has been tailored to low- pressure CVD(LPCVD) batch processing in the microelectronics industry. In this case, a specialized support holds a large number(over a hundred) of closely-spaced silicon wafers for simultaneous processing. In general, hot wall reactors have the advantages of being able to process large batches of substrate, and having relatively uniform substrate temperatures and thus coating thickness. The primary disadvantages are that the walls get heavily coated, frequent cleaning and causingrequiring problems, and that it involvesparticle higher thermal loads and energy usage.

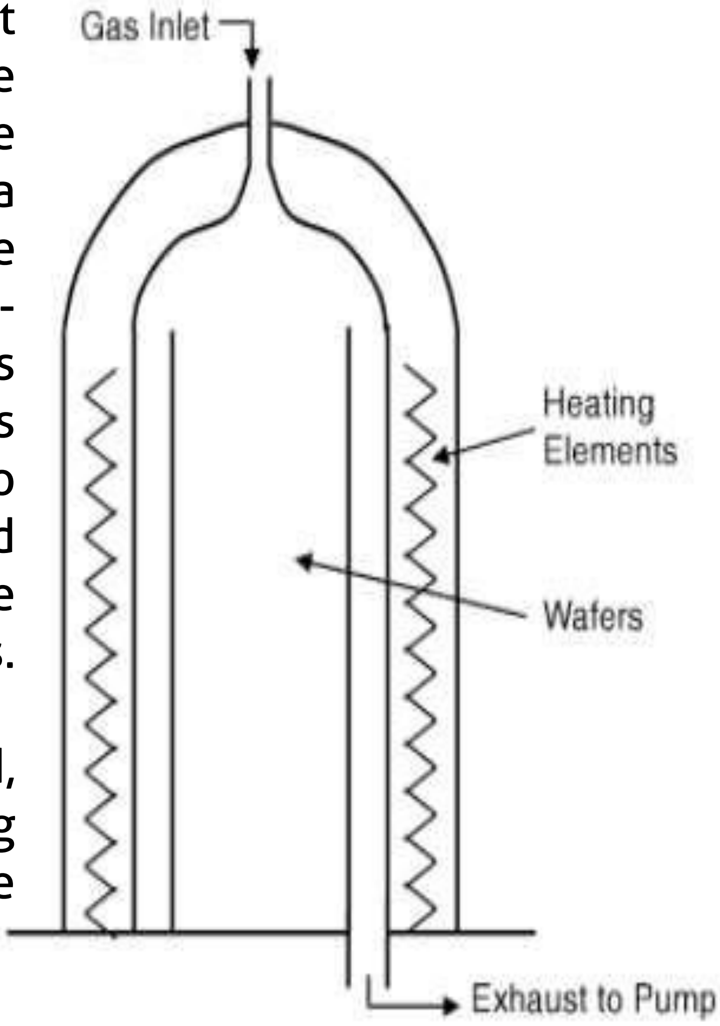


Fig. 8: Schematic drawing of LPCVD furnace for batch processing of multiple silicon wafers.

On the other hand, in a Cold-wall reactor only the substrate is heated, either resistively or inductively. In such systems, the substrates are heated but the walls are cooled. Cold wall reactor often run at relatively high pressures, several hundred torr to atmospheric total pressure, and usually have reactive precursors diluted in a carrier gas.Figure 9 shows an example of a Cold wall rotating disk CVD reactor. This system has water-cooled quartz walls, with a rotating holder for(silicon or compound semiconductor) wafers that is resistively heated. Most compound semiconductor CVD processes use reactors of this type. Cold wall reactors have the advantages of reduced deposition of material on the walls, which means less cleaning, lower thermal loads on the substrates because of faster heat-up and the avoidance of vacuum equipment. The primary disadvantages are larger temperature non-uniformities on the substrate, which may lead to film thickness non- uniformities, the smaller batch sizes.

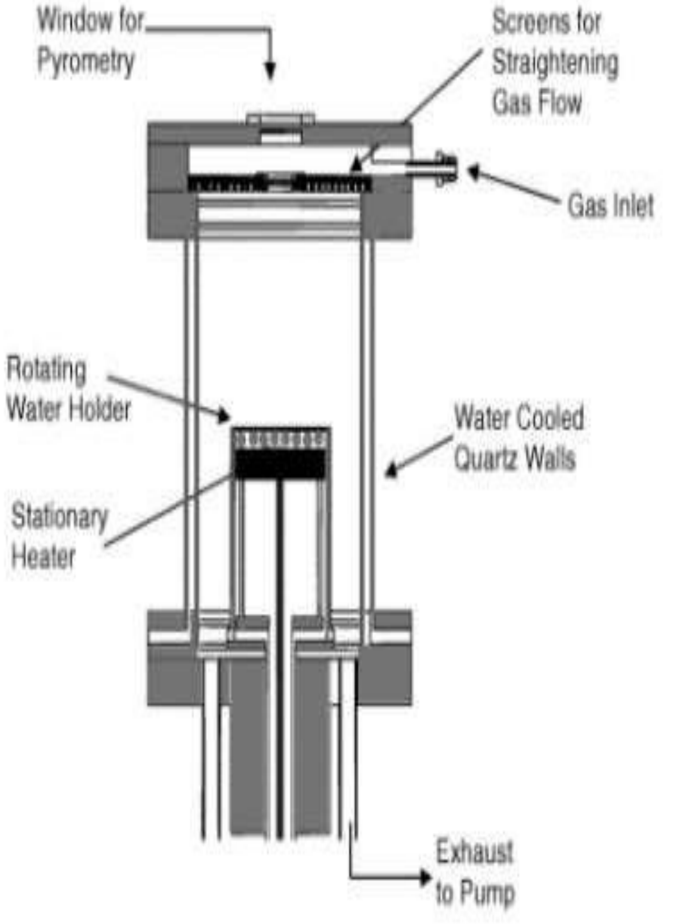
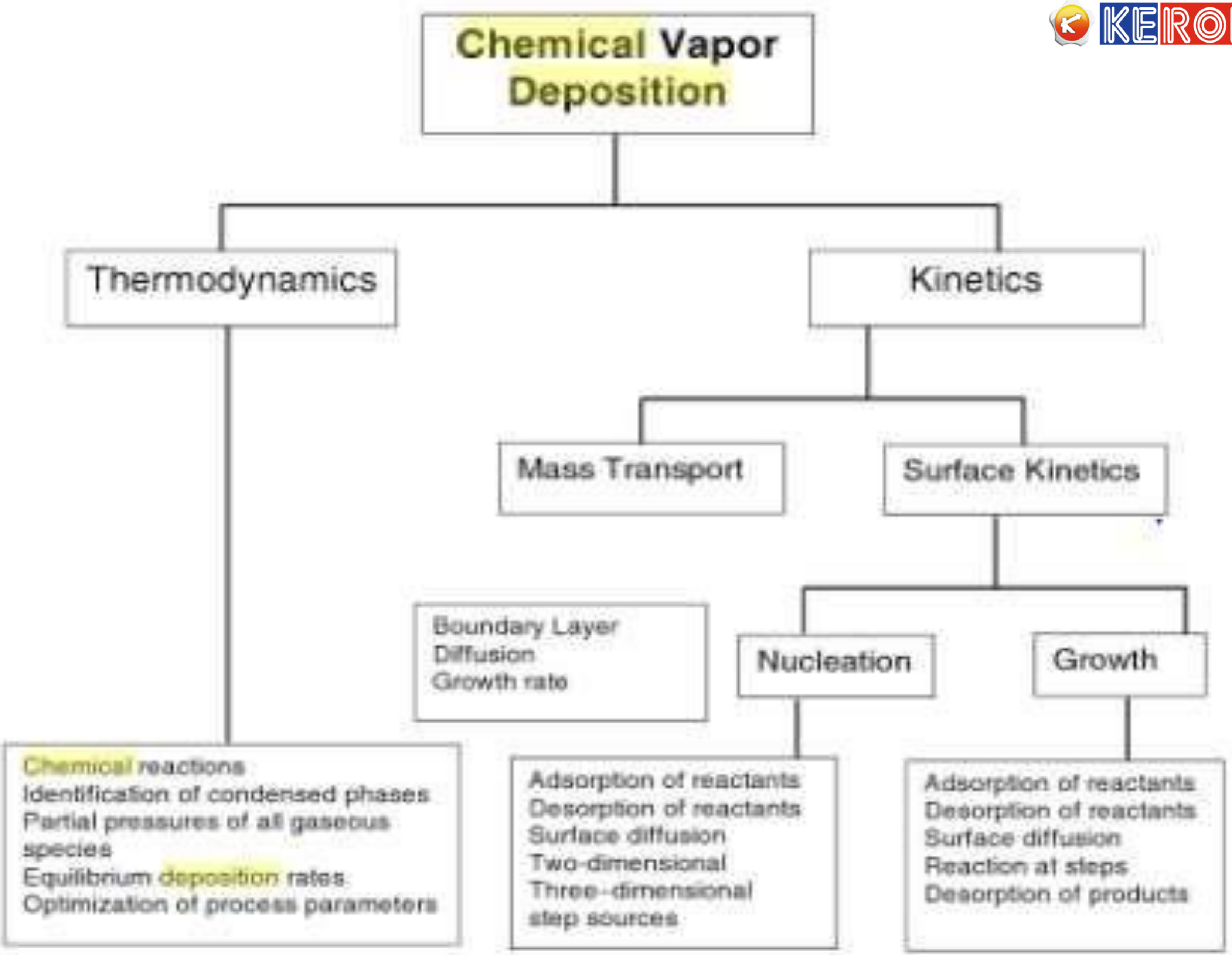


Fig. 9: Schematic diagram of a cold-wall rotating disk CVD reactor used for depositing thin films on semiconductor wafers.



Chemical Vapor Deposition

Thermodynamics

Kinetics

Mass Transport

Surface Kinetics

Boundary Layer
Diffusion
Growth rate

Nucleation

Growth

Chemical reactions
Identification of condensed phases
Partial pressures of all gaseous species
Equilibrium deposition rates
Optimization of process parameters

Adsorption of reactants
Desorption of reactants
Surface diffusion
Two-dimensional
Three-dimensional
step sources

Adsorption of reactants
Desorption of reactants
Surface diffusion
Reaction at steps
Desorption of products

Fig. 1: Various fundamental aspects involved in a chemical vapor deposition process.

Deposition Mechanism:

The manner in which a film is formed on a surface by CVD is still a matter of controversy and several theories have been advanced to describe the phenomena. Figure 10 shows the seven mechanistic steps that have been hypothesized to occur during a vapor deposition process.

These steps include:

1. Transport of reactant gases into the reaction chamber,
2. Intermediate reactants form from reactant gases,
3. Diffusion of reactant gases through the gaseous boundary layer to the substrate,
4. Absorption of gases onto the substrate surface,
5. Single or multi-step reactions at the substrate surface,
6. Desorption of product gases from the substrate surface, and
7. Forced exit of product gases from the system.

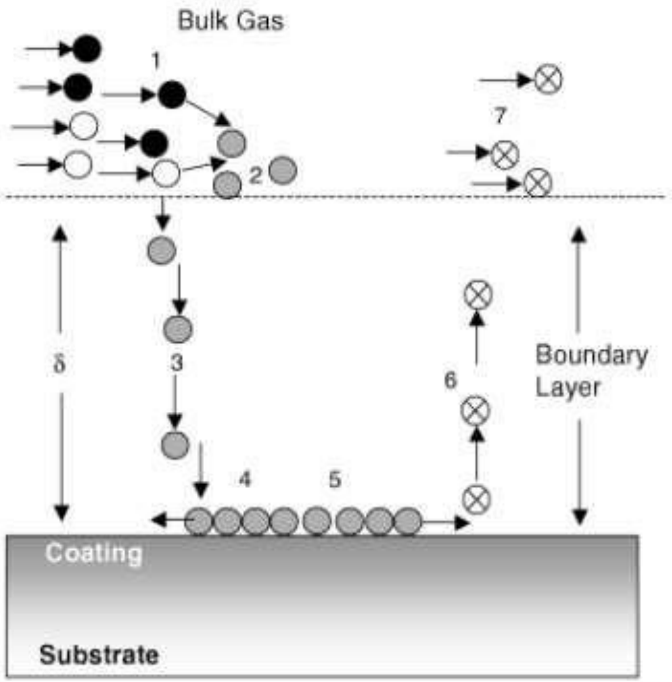


Fig. 10: Schematic diagram of the mechanistic steps that occur during the CVD process.

In this model, the steps can be classified into two categories, mass transport and surface reaction steps.[2,4,5 and 6] The lowest of these steps determines if the process is mass transport or surface reaction limited. As the temperature increases, the surface reaction rate rises exponentially, resulting in a mass transport limited because transport becomes the slowest step in the series deposition steps.

A thermodynamics theory proposes that a solid nucleus is formed from supersaturated vapor as a result of the difference between the surface free energy and the bulk free energy of the nucleus. Another and new theory is based on atomistic nucleation and combines chemical bonding of solid surfaces and statistical mechanics.

There are however, three important factors that control the nature and properties of the deposit to some degree which must be reviewed at this time: epitaxy, gas-phase precipitation, and thermal Expansion.

1. **Epitaxy:**

A specific case is that of epitaxy where the structure of the substrate essentially controls the structure of the deposit.[2] Epitaxy can be defined as the growth of a crystalline film on a crystalline substrate, with the substrate acting as a seed crystal. When both substrate and deposit are of the same material(for instance silicon on silicon) or when their crystalline structure(lattice parameters) are identical or close, the phenomena is known as homoepitaxy. When the lattice parameters are different, it is heteropitaxy. Epitaxial growth can't occur if these structural differences are too great.

2. **Gas Phase Precipitation:**

As mentioned previously, a CVD reaction may occur in the gas phase instead of at the substrate surface if the super saturation of the reactive gases and the temperature are sufficiently high. This is generally detrimental because gas-phase precipitated particles, in the form of soot, become incorporated in the deposit, causing non-uniformity in the structure, surface roughness and poor adhesion. In some cases, gas-phase precipitation is used purposely, such as in the production of extremely fine powders.

Thermal Expansion:

Large stress can be generated in a CVD coating during the cooling period from deposition temperature to room temperature, if there is a substantial difference between the coefficient of thermal expansion (CTE) of the deposit and that of the substrate. These stresses may cause cracking and spalling of the coating. If differences are large, it may be necessary to use a buffer coating with in intermediate CTE or with high ductility. Deposition processes which do not require high temperatures, such as MOCVD or plasma CVD, should also be considered.

Example; As an example, one can consider the deposition of tungsten on the interior wall of a graphite tube by the hydrogen reduction of the fluoride as follows,

$$WF_6 + 3H_2 \rightarrow W + 6HF$$

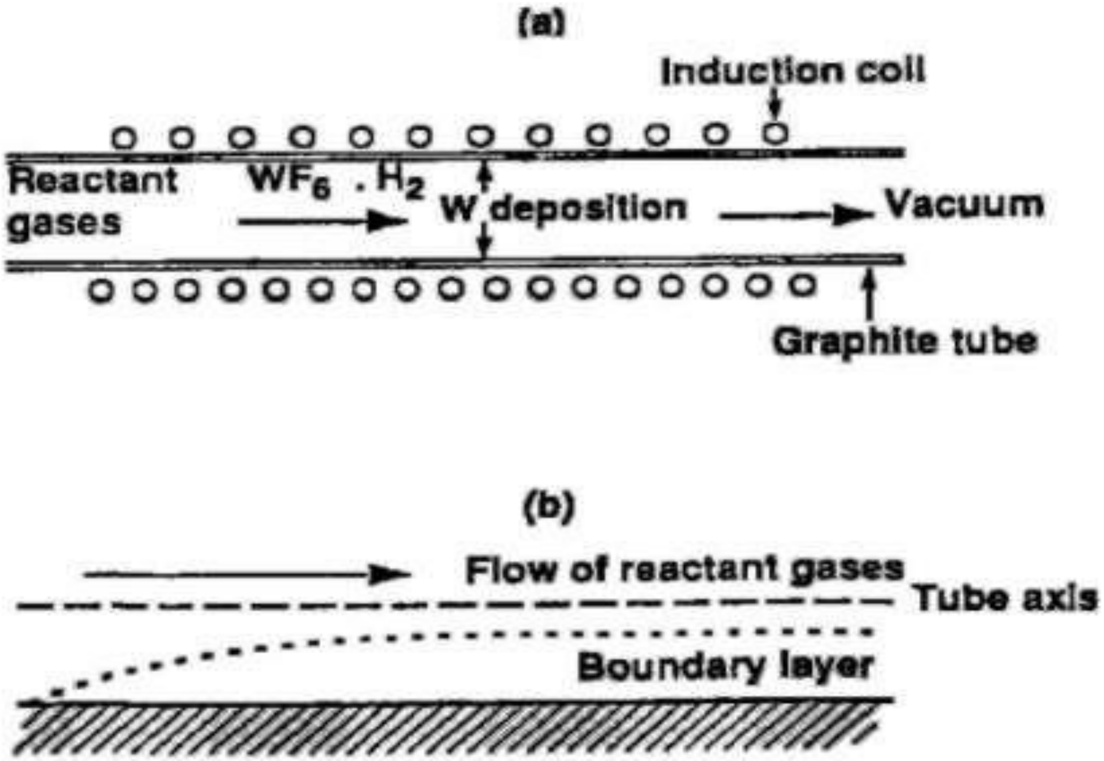


Figure 2.4. *(a)* Tungsten deposition in a tubular reactor, *(b)* boundary layer conditions.

A sequence of physic-chemical process steps take place in a CVD process. First the reagents have to the surface being coated. The zone between the bulk of the flowing gas and the substrate surface is the location of the 1st kinetics barrier, which has to be crossed by diffusion of gaseous species. Next the species are adsorbed on the substrate surface, and migrate, react and the product to be deposited is formed to form nuclei.

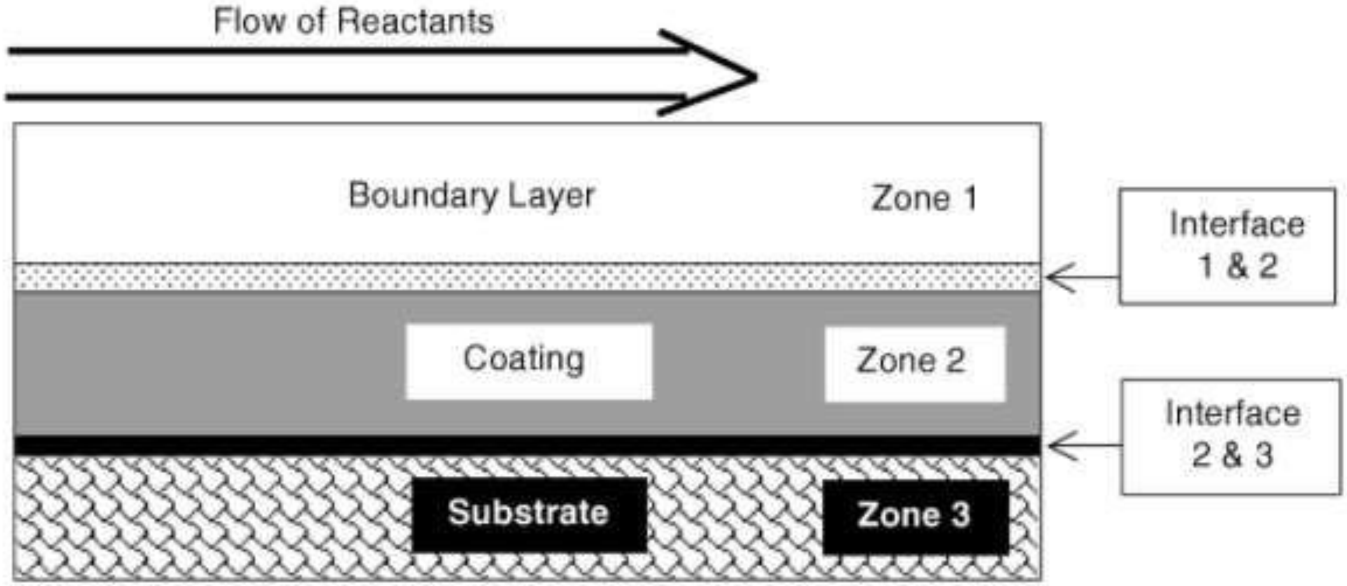


Fig. 2: A schematic diagram of the boundary layer model showing the reaction zones for Al_2O_3 coating.

In the case of laminar flow which is typically assumed in all models and calculations, the gas velocity is zero at the substrate surface and increase to a constant value (the bulk gas flow velocity) at some distance from the substrate. Boundary layer theory (BLT) provides the key to understanding the dynamics of these surface reactions. It can help couple the chemical and mass transport processes occurring near or on the heated substrate surface as gas flows over it. For fluid dynamics reasons a more or less stagnant boundary layer occurs in the vapor adjacent to the substrate/coating interface. During the coating process, the gaseus reactants and products are transported across reaction zone-1(fig 2) as well as in the main gas stream, where homogeneous nucleation in the vapor can occur.

These reactions are usually undesirable, and can lead to flaky and\or non- adherent coatings. Heterogeneous reactions, which in many system determine growth rate, occur at the interface between zones 1 and 2(vapor/coating). The typically high temperatures used in CVD can and do lead to various solid state reactions (i.e. phase transformations, grain growth) during the deposition process in zones 2 and 3(coating and the substrate). At the interface between these zones (2 and 3) diffusion can result in the formation of various intermediate phases, which are of importance to the adherence characteristics of the coating.

Advantages:
CVD has a number of advantages as a method for depositing thin films. One of the primary advantages is that the film thickness on the sidewalls of features is comparable to the thickness on the top. This means that films can be applied to elaborately shaped pieces, including the insides and undersides of features. Another advantage of CVD is that, in addition to the wide variety of materials that can be deposited, they can be deposited with very high purity. Other advantage include relatively high deposition
rates, and the fact that CVD often doesn't require as high a
vacuum as PVD processes.

Disadvantages:
CVD also has number of disadvantages. One of the primary disadvantage lies in the properties of the precursors. CVD precursors can also be highly toxic, explosive, or corrosive. The byproducts of CVD reactions can also be hazardous. The major disadvantage is the fact that the films are usually deposited at elevated temperatures. This put some restrictions on the kind of substrates that can be coated.

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