A Brief Insight on Chemical Vapor Deposition Processes

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Abstract

Processing of the electronic materials for electronic and optoelectronic devices, advanced materials for bio and space research, combines a fascinating variety of physical transport processes and chemical reactions that raise new challenges to “chemical reaction engineering”. The rapid and extensive growth in microelectronics and space technology owes much to the scientists and engineers concerned with solving materials and processing materials associated with achieving new device structures and ever-higher levels of integration. Fabrication of these components involves a variety of complex chemical processes, which can be divided into the unit operations like “Bulk crystal growth, Liquid phase epitaxy, Physical vapor deposition, Chemical vapor deposition, packaging etc…. Among these “Chemical vapor Deposition” (CVD) is perhaps the only fabrication processes that lend itself most easily to chemical reaction engineering analysis. This atomistic deposition method can provide heavy metals with structural control at atomic and nanometer scale level. This is a review paper which gives a brief view of the fundamental aspects of “Chemical vapor Deposition” (CVD), kinetics and deposition mechanism. Along with these this paper also reviews the different types of chemical vapor deposition processes, which are based on the type of precursors used and different heating methods. The recent applications of CVD in microelectronic fabrication, coating of metals, bio-compatible materials and advanced material technology, the advantages and limitations of CVD are also discussed.

Keywords: Chemical Vapor Deposition, Kinetics, Thin Films, Reaction Engineering

I. INTRODUCTION

Starting with the announcement of the transistor in 1948 and the introduction of planar transistor in 1959 the microelectronics industry has undergone an impressive evolution to current state where microelectronics circuits are essential almost all aspects of modern society. For the last 25 years the number of components in the most advanced integrated circuits has doubled every year to the present level of 106 transistors on a chip. Compound semiconductors such as GaAs, AlGaAs and GaInAsP find increasing use in high speed electronic devices and optoelectronic components. The later technology is critical for fiberoptic communication and future optical computing and storage systems. With its versatility CVD has become one of the main processing methods for wide range of applications including metallic films (Ir, Rh..) for rocket engine components, porous structures (Ta, Ni, Zr, Ti..) for biocompatible materials, refractory ceramic materials (ZrO2, TiN, SiC..) for protection against corrosion and this technique could play a significant role in advance fabrication techniques.

A. Chemical Vapor Deposition:

Chemical vapor deposition (CVD) is the microelectronic fabrication process that lends itself most easily to chemical reaction engineering analysis. As the name indicates, chemically reacting gases are used to synthesize a thin solid film. Homogeneous as well as heterogeneous reactions may be involved in film growth. The chemical reactions involved in CVD distinguish it from physical deposition processes, such as sputtering and evaporation. Chemical vapor deposition is usually defined as a process involving one or more chemical reactions which transform gaseous molecules, called precursors, in to a solid material in the form of thin film or powder on the surface of a substrate.

B. Fundamental reactions Step of CVD:

1) Vaporization and transport of precursor molecules in to the reactor.
2) Diffusion of precursor molecules to the surface.
3) Adsorption of precursor molecules on the surface.
4) Decomposition of precursor molecules on surface and incorporation into solid films.
5) Recombination of molecular by products and desorption into gas phase.

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C. Chemical Vapor Deposition Essentials

1) CVD precursors:

a) Volatility:
   vapor pressure – simple molecules with high vapor pressure are rare. Determined by molecules weight and molecularity (degree polymerized) which is a result of structure and bonding.

b) Stability, Reactivity and Safety:
   Bond strength, bond dissociation energy which affects process, temperature and film composition (purity), thermal stability in storage and delivery in to the reactor, reactivity of precursor and byproducts towards other substances (including biological objects) are some of the general considerations.

c) Single Source Precursor:
   It has the advantages like simpler delivery system, uniform elemental distribution at atomic level, limited composition range. Hydrides like SiH4, GeH4, AlH3, PH3…, halides like TiCl4, TaCl5, MoF6, WF6, metal-organics like metal alkyls, metal alkoxides, metal diketonates, metal carboxyls… are some of the commonly used precursors in chemical vapor deposition.

2) CVD Energy Sources:
   Various types of energy sources can be used for the heating substrate layers. In thermal energy by using resistive heating (tube furnace), radiant heating (quartz Tungsten halogen lamp) which is a very good heat source, inductive heating (radio frequency), laser energy, heat can be supplied. Along with these UV-visible light, laser as photo energy which comes under photo energy and glow discharge which is also called as plasma can also be used for heating purpose. At present lot of research is going on glow discharge. By using glow discharge processes can be done at low temperatures. These are discussed later in different types of chemical vapor deposition.

3) CVD Reactors
   Before designing reactor for chemical vapor deposition we have to consider some general system requirements like gas vapor delivery lines, materials of construction/geometry, substrate loading and unloading assembly, energy sources (RF, Plasma…), plasma control and measurement gauges (gas flow rate, pressure, temperature, deposition time), safety equipment (alarms, sensors…).
   There are two differences between the CVD reactors and the usual chemical reactors [Klavs F.Jensen, (1987)]
   1) In CVD reactors, NO recycle is used, partly because of the impurities that such a recycle stream can introduce and partly because of strict requirements on the controllability of the desired gas phase composition.
   2) The flow regimes in CVD reactors can be diverse, depending on the pressure, temperature, and flow rate. Chemical reactors usually operate in the turbulent regime.

a) Regimes of Fluid Flow:
   For a typical CVD operation, the Reynolds number is around 100 or less. Thus the flow regime in CVD reactors is laminar unless buoyancy due to temperature gradient causes eddies. Flow should be fully developed before it reaches the susceptor. In CVD process one important assumption is made i.e. the fluid is incompressible. The assumption of incompressible fluid is very reasonable when the flow velocity is much less than the sound velocity (3.35*104cm/s), which is more than satisfied for CVD reactors where fluid flow velocity is less than 100cm/s. Another assumption to be made is constant physical properties for fluid in the reactor.

II. CVD Reactor Kinetics

CVD data have traditionally been reported in terms of growth rates and their dependence on temperature. Because of high temperatures and low pressures used in CVD, care has to be taken in using the reported gas phase rate constants. It is relatively easy to understand the difference between mass transfer and surface reaction when the deposition follows first order kinetics. At steady state, the rate of mass transfer from bulk fluid to the substrate surface should be equal to the rate of deposition.

\[ K_m (C_b → C_s) = r_G = k_C \]

For first order kinetics, surface concentration is given by: \( C_s/C_b = k_m / (k_s + k_m) \) and the rate of deposition is given by \( r_G = k_m C_b \). If \( k_s \gg k_m \), the rate of deposition is simply given by \( k_m C_b \). When the condition is satisfied, the resistance to mass transfer (1/k_m) is much larger than the resistance to reaction (1/k_s), which means deposition is controlled by mass transfer. Therefore in this case deposition rate is almost independent of temperature since the mass transfer coefficient is a weak function of temperature.

In the other extreme where \( k_s \ll k_m \), the chemical kinetics controls the deposition, and the deposition rate becomes heavily dependent on temperature, because of the Arrhenius (exponential) temperature dependence of the rate constant. In this case the rate \( r_G \) becomes simply \( k_s C_s \). It is often stated that mass transfer controls if the rate of mass transfer is much smaller than the rate of deposition and vice-versa. The question whether mass transfer or surface reaction is rate limiting can always resolved, even
without knowledge of the kinetics, provided the actual deposition is known \((rG)_m=\text{Measured rate of deposition. Surface kinetics controls if (rG)} \) m/kmCs<<1 and Mass transfer controls if (rG) m/kmCs=1.

1) Controlling of the Film Thickness:
This can be explained by taking the deposition of situ phosphorous doped polycrystalline Si as an example. It involves a slow gas phase reaction followed by a very rapid surface reaction, which explains the low but highly non-uniform growth rates. If the contribution from the flow region could be eliminated, the growth would be uniform, albeit low. This can be done by placing quartz cages around the wafers which capture the SiH₂. As shown in the figure there is an optimal cage area. If the area is too small insufficient SiH₂ is retained. On the other hand, if the area is too large SiH₂ is depleted from the wafer region so the deposition profile reverses and is thickest in the centre region. This combination of detailed chemical kinetics and transport modelling [Jensen et al., (1985)] should offer challenging chemical engineering problems.

### III. Different Types of CVD Processes

#### A. Plasma Enhanced Chemical Vapor Deposition:
Plasma enhanced CVD (PECVD) reactors are extensively used in “Microelectronics processing” for deposition. The considerable interest in plasma deposition is driven by the ability to grow films at relatively low process temperatures combined with special material properties that cannot be realized in conventional thermally driven process [Dubach, et al., (1997)]. Increasing ion bombardment tends to make films denser and cause the film stress to become more compressive. These plasma are also called glow discharges, are generated by applying an external electrical field to the process gas at low pressures (1-500 Pa). The electrodes may be parallel plates or an external coil. Both DC and radio frequency sources (40 kHz-40 Mhz) are used. In typical capacitive plasma the electron temperature might be 3 ev. The ion and neutral temperatures are much smaller. As shown in Table 1, the No. of electrons with sufficient energy to dissociate a molecule is 10 to 100 times larger than the No. that can ionize. The plasma will produce a large supply of excited and dissociated molecules and thus reactive radicals, even for a modest fractional ionization. Final important benefit of plasma deposition is the ability to easily clean the reactor. Table 2 shows the temperature differences between thermal CVD and PECVD.

<table>
<thead>
<tr>
<th>Process gas</th>
<th>Dissociation Energy</th>
<th>Ionization Energy</th>
<th>No/ N²</th>
</tr>
</thead>
<tbody>
<tr>
<td>H₂</td>
<td>4.5 ev</td>
<td>15.4 ev</td>
<td>38</td>
</tr>
<tr>
<td>O₂</td>
<td>5.2 ev</td>
<td>12.0 ev</td>
<td>9.6</td>
</tr>
<tr>
<td>CH₄</td>
<td>4.5 ev</td>
<td>12.6 ev</td>
<td>15</td>
</tr>
<tr>
<td>F₂</td>
<td>1.6 ev</td>
<td>15.7 ev</td>
<td>109</td>
</tr>
</tbody>
</table>

#### B. Laser Chemical Vapor Deposition:
This process is analogous to thermally driven CVD, but instead of a diffusing heating source a focused laser beam is used to define deposition areas spatially. The laser has the added advantages of an increased energy flux and rapid heating. In order to avoid photochemistry, the radiation must be chosen so that gas is transport to laser beam. Its main advantage is it is very handy when we want to deposit on specific areas. Direct laser writing of insulators, semiconductors and metal is a very active area of application. One major advantage of this process is it is very difficult to measure the temperature in the irradiated spot. It is not fully understood.

#### C. Photo Chemical Vapor Deposition:
Photosensitization is used in wide area photochemical vapor deposition. Hg vapor is usually used as a sensitizer. It is readily excited by an external Hg-lamp according to:Hg+hv →Hg*. It is subsequently transferred to other gas phase species by collision with Hg*. This process is used commercially for depositing low temperature SiOₓ and SiNₓ from SiH₄, N₂O and NH₃, respectively [Rathi et al., (1995)].
D. Metal-Organic Chemical Vapor Deposition:

Metal-organic CVD has attracted considerable attention because it allows synthesis of thin, high purity epitaxial films of compound semi-conductors for new optoelectronic and high speed electronic devices [Yang et al., (1997)]. These optoelectronic components play a key role in optical communication, storage and computing as well as in defense systems. By varying the constituents and their concentration in the semiconductor, it is possible in principle to obtain sensors with wavelengths ranging from the visible to the far infrared.

E. Low Pressure Chemical Vapor Deposition:

LPCVD processes typically involve several reactants with little or no dilution and the deposition is associated with significant volume changes. The range of total pressure in a typical LPCVD process ranges between 0.01-0.1 KPa. Because of low pressure the fluid velocity in the LPCVD reactor is higher by an order of magnitude than the velocity in the atmospheric CVD. This process yields a better thickness uniformity but at the cost of a lower deposition rate when compared with the atmospheric CVD. Because of this advantage only it is widely used. Another advantage of LPCVD is the reduction in undesired impurities. This process is the main production tool for “polycrystalline Si, dielectric and passivation films used in Si IC manufacturing.

IV. ADVANTAGES AND APPLICATIONS OF CVD

A. Advantages:

CVD offers many advantages over other deposition processes. Key advantage of the CVD process lies in the fact that the reactants used are gases, thereby taking advantage of the many characteristics of gases. CVD is not a line-a-sight process as are most other plating/coating processes. It is a versatile process because in this precursors are able to penetrate porous bodies, blind holes, large L/D tubes, etc. so that we can deposit any element or compound. This process gives high purity, typically 99.99-99.999%. With this deposition technique we can get 100% of theoretical density and material formation will be below the melting point. A wide variety of thin films with good control of composition, surface morphology, thickness, and step coverage can be formed. Since many parts can be coated at the same time this process is very economical in production and it can be operated at a wide range of temperatures and pressures.

B. Applications:

CVD process is widely used in electronic applications like processing of semiconductors, conductors, insulators, diffusion barriers, Opto- electronic and Ferro electronic fields, Integrated chip manufacturing and preparation of biocompatible materials. Coatings are the most common applications of CVD. It generally fall into two categories i.e. conversion coating and deposited coating. Normally coatings are applied to provide wear, corrosion, and erosion protection. When coating is made sufficiently thick, the substrate can be removed to create a free standing, monolithic part. CVD process can also be applied in advanced material technology like fabrication of rocket engine components, Ir/Rh thrust chambers, Ir/Rh solid propellant throats and other gas flow components, porous media (Filtration, catalysts, noise reduction), light weight precision optical reflectors, Armor penetrating warheads and also in composite technology.

V. CONCLUSION

There are clearly many opportunities for reaction engineering to play a role in advancing material processing technology. This paper has emphasized that Chemical Vapor Deposition is the area where reaction engineering concepts already have been utilized productively and additional applications can readily be envisioned. Finally it should be stressed that processing of advanced materials is an highly interdisciplinary field. Therefore, for reaction engineering to address significant problems, it is essential to understand the goals and concerns of electrical engineers, physicists and material scientists working on new device structures and concepts.

REFERENCES