F4280 Technologie depozice tenkých vrstev a povrchových úprav - kap. 5

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5.1 Gaseous Sources

Let's use practical distinguishment of gas and vapor: gas does not condense when held above room T and below 1-atm partial pressure.

Distinguishing the methods of delivery according to equilibrium vapor pressure p_v:

- sources species having $p_v < 10^{-2}$ Pa at the wall T of the deposition chamber must by "physically" evaporated (using heat or energy beams) $\Rightarrow$ PVD processes (requiring low-p operation and "line-in-sight" geometry

- materials with $p_v > 10^{-2}$ Pa at the wall T are used in CVD (can operate at atmospheric pressure or lower - fluid flow $K_n \ll 1$)

Most of elements, with exception of alkali metals and alkaline earths (group IA and IIA) can be converted to gases or to chemical vapors by reacting them with terminating radicals, e. g.

- H
- halogens F, Cl, Br, I
- carbonyl CO
- H-saturated organic radicals R such as methyl CH_3 and ethyl CH_2CH_3

5.2 Chemical Vapor Deposition

. . . constituents of the vapour phase react chemically near or on a substrate surface to form a solid product. Most CVD processes are chosen to be **heterogenous** reactions. Undesirable **homogeneous** reactions in the gas phase nucleate particles that may form powdery deposits and lead to particle contamination.
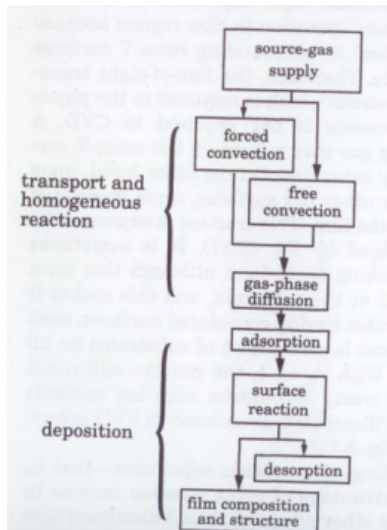
5.3 Chemical Reactions in CVD

TABLE 7.1 Typical Overall Reactions Used in CVD

pyrolysis (thermal decomposition)	$SiH_4(g) \rightarrow Si(c) + 2H_2(g)$
	$SiH_2Cl_2(g) \rightarrow Si(c) + 2HCl(g)$
	$CH_4(g) \rightarrow C(\text{diamond or graphite}) + 2H_2(g)$
	$Ni(CO)_4(g) \rightarrow Ni(c) + 4CO(g)$
oxidation	$SiH_4(g) + 2O_2(g) \rightarrow SiO_2(c) + 2H_2O(g)$
	$3SiH_4(g) + 4NH_3(g) \rightarrow Si_3N_4(c) + 12H_2(g)$
hydrolysis	$2AlCl_3(g) + 3H_2O(g) \rightarrow Al_2O_3(c) + 6HCl(g)$
reduction	$WF_6(g) + 3H_2(g) \rightarrow W(c) + 6HF(g)$
displacement	$Ga(CH_3)_3(g) + AsH_3(g) \rightarrow GaAs(c) + 3CH_4(g)$
	$ZnCl_2(g) + H_2S(g) \rightarrow ZnS(c) + 2HCl(g)$
	$2TiCl_4(g) + 2NH_3(g) + H_2(g) \rightarrow TiN(c) + 8HCl(g)$

Materials deposited at low temperatures (bellow 600 °C for silicon) are generally
amorphous. Higher temperatures tend to lead to **polycrystalline** phases. Very high
temperatures (typically 900–1100 °C in the case of silicon) are necessary for growing
single-crystal films.

Complex Reactions - Polymerization

5.4 Deposition Variables

temperature, pressure (from low pressures, i.e., 10–1000 Pa - LPCVD, up to atmospheric pressures - APCVD), input concentration, gas flow rates, reactor geometry, operating principles. Kinetics of the reactions may depend on such factors like substrate material, structure and orientation.

5.5 Chemical Reactors

Chemical reactors must provide several basic functions:

- ▶ transport of the reactant and diluent gases to the reaction site,
- ▶ provide activation energy to the reactants (heat, radiation, plasma),
- ▶ maintain a specific system pressure and temperature,
- ▶ allow the chemical processes for thin film deposition to proceed optimally,
- ▶ remove the by-product gases and vapours.

Reactor geometry affects the gas flow characteristics which, in turn affect the properties of the deposited layer. Two basic flow type reactors:

- ▶ Displacement or **plug flow reactor** in which the entering gas displaces the gas already present with no intermixing of successive fluid elements. Plug flow is a simplified and idealized picture of the motion of a fluid, whereby all the fluid elements move with a uniform velocity along parallel streamlines. Mass balance for reactant A involved in a single reaction is very simple: $F_A - (F_A + dF_A) = r_A dV$.
- ▶ **Perfectly mixed flow reactor** is the opposite extreme from the plug flow reactor. To approach the ideal mixing pattern, the feed has to be intimately mixed with the contents of the reactor in a time interval that is very small compared to the mean residence time of the fluid flowing through the vessel. The essential feature is the assumption of complete uniformity of concentration and temperature throughout the reactor.

5.6 Different CVD Techniques

▶ CVD epitaxy (see next chapter in presentation) and metal-organic CVD (MOCVD - see Handbook of Thin Film Deposition, ed. S. Krishna, chapter 4.)
CVD epitaxy or vapour-phase epitaxy (VPE) and metal-organic chemical vapour deposition (MOCVD) are used for growing epitaxial films of e.g. silicon or compound semiconductors. Layers of accurately controlled thickness and dopant profile are required to produce structures of optimal design for device fabrication.

▶ low pressure and atmospheric pressure CVD
These two methods are used for deposition of polycrystalline or amorphous materials like polysilicon, silicon nitride and low temperature oxide (LTO).

▶ ALD

5.7 APCVD and LPCVD

The deposition of thin films for semiconductor device manufacture by CVD at atmoshperic pressure (APCVD) was a widely accpeted process in 1976 when equipment for low-pressure CVD (LPCVD) was introduced into the marketplace. At that time, the 3-inch wafer was the predominantly wafer size used in production with some residual presence of smaller wafers and the 4-inch wafer just being introduced into advanced lines.

In the next few years, the LPCVD process became the preferred method for chemical vapour deposition of thin films. The transformation to a new technology that required massive capital expenditure for new equipment took place at a rapid rate throughout the industry. The reason for this rapid change were: (1) a superior film quality, (2) a greatly reduced processing cost, and (3) greatly increased thtoughput per unit of capital investment. Improved film quality also means increased yields and decreased unit costs in an industry that was becoming increasingly competitive.

5.8 MOCVD

5.9 Atomic Layer Deposition

https://www.youtube.com/watch?v=HUsOMnV65jk This example shows the ALD chemistry for producing HfO2 from gaseous precursors HfCl4 (Cl=green) and H2O (O=red). ALD allows a uniform coating to be applied to complex objects - such as the inside of the fibre optic cable shown here.

https://www.youtube.com/watch?v=XMda8TXLIFk Deposition of TiO_2 using TiCl4 and H2O

5.10 Thermal Forming Processes

In the gas phase, **thermal oxidation and nitridation** is a chemical thin-film forming process in which the **substrate itself provides the source for the metal or semiconductor constituent** of the oxide and nitride, respectively. This technique is obviously much more limited than CVD.

The **thermal oxidation**

- ▶ extremely important applications in Si device technology (very high purity oxide films with high quality Si/SiO_2 interface are required).
- ▶ **Thermal oxidation of silicon** surfaces produces glassy films of SiO_2 for protecting highly sensitive p-n junctions and for creating dielectric layers for MOS devices.
    - ▶ $T = 700 - 1200 \ \circ C$
    - ▶ dry oxygen or water vapour (steam) as the oxidant; steam oxidation proceeds at a much faster rate than dry oxidation
    - ▶ The oxidation rate is a function of the oxidant partial pressure and is controlled essentially by the rate of oxidant diffusion through the growing SiO_2 layer interface, resulting in a decrease of the growth rate with increased oxide thickness.
    - ▶ The process is frequently conducted in the presence of hydrochloric acid vapours or vapours of chlorine-containing organic compounds. The HCl vapour formed acts as an effective impurity getter, improving the Si/SiO_2 interface properties and stability.
    - ▶ **Si oxidation under elevated pressure** is of technological interest where the temperature must be minimized (VLSI devices): oxidation rate of silicon is $\approx p \Rightarrow$ higher product throughput and/or decreased temperatures. Oxidant: H2O, p up to 10 atm, T usually 750–950 $^\circ$C.

Gas-phase **oxidation of other materials** is of limited technical importance. Examples: metallic Ta films converted by thermal oxidation to tantalum pentoxide for use as antireflection coating in photovoltaic devices and as capacitor elements in microcircuits. Other metal oxides grown thermally: capacitor dielectrics in thin-film devices, improve the bonding with glass in glass-to metal seals, improve corrosion resistance.