Lecture-9
Chemical Vapor Deposition

Two-Dimensional Nanostructures Cont…
(Ref: Guozhong Cao; Nanostructures & Nanomaterial: Synthesis, Properties & Applications)
Chemical Vapor Deposition (CVD)

- Substrate Exposed to Volatile Precursors
- Precursors react/decompose on substrate
- Desired film/powder deposited on substrate
- Extensively studied and well documented
- Close association with solid-state micro-electronics
Typical Chemical Reactions

• Homogeneous & Heterogeneous reactions are intricately mixed.

• Gas phase homogeneous reaction prevails:
  (i) Increasing Temperature
  (ii) Partial Pressure of Reactants
Gas phase reactions predominates with:

(i) Extremely high concentration of Reactants

It leads to Homogeneous Nucleation

For good quality films deposition:

- Homogeneous nucleation should be avoided.
Chemical reactions can be grouped into:

(A) Pyrolysis or thermal decomposition

\[ \text{SiH}_4(g) \rightarrow \text{Si}(s) + 2\text{H}_2(g) \text{ at } 650^\circ\text{C} \]

\[ \text{Ni(CO)}_4(g) \rightarrow \text{Ni}(s) + 4\text{CO}(g) \text{ at } 180^\circ\text{C} \]

(B) Reduction

\[ \text{SiCl}_4(g) + 2\text{H}_2(g) \rightarrow \text{Si}(s) + 4\text{HCl}(g) \text{ at } 1200^\circ\text{C} \]

\[ \text{WF}_6(g) + 3\text{H}_2(g) \rightarrow \text{W}(s) + 6\text{HF}(g) \text{ at } 300^\circ\text{C} \]
(C) Oxidation

\[ \text{SiH}_4(g) + \text{O}_2(g) \rightarrow \text{SiO}_2(s) + 2\text{H}_2(g) \text{ at } 450^\circ\text{C} \]

\[ 4\text{PH}_3(g) + 5\text{O}_2(g) \rightarrow 2\text{P}_2\text{O}_5(s) + 6\text{H}_2(g) \text{ at } 450^\circ\text{C} \]

(D) Compound Formation

\[ \text{SiCl}_4(g) + \text{CH}_4(g) \rightarrow \text{SiC}(s) + 4\text{HCl}(g) \text{ at } 1400^\circ\text{C} \]

\[ \text{TiCl}_4(g) + \text{CH}_4(g) \rightarrow \text{TiC}(s) + 4\text{HCl}(g) \text{ at } 1000^\circ\text{C} \]
(E) Disproportionation

\[ 2\text{GeI}_2(g) \rightarrow \text{Ge}(s) + \text{GeI}_4(g) \text{ at } 300^\circ\text{C} \]

(F) Reversible Transfer

\[ \text{As}_4(g) + \text{As}_2(g) + 6\text{GaCl}(g) + 3\text{H}_2(g) \]
\[ \rightarrow 6\text{GaAs}(s) + 6\text{HCl}(g) \text{ at } 750^\circ\text{C} \]
• Demonstration of versatile chemical nature of CVD

• For deposition of given film
  
  - Different reactants/precursors can be used
  
  - Different chemical reactions may apply

• E.g.
  
  - Silica films may be synthesized by different ways:
Different ways to achieve silica-film:

a) $\text{SiH}_4(g) + \text{O}_2(g) \rightarrow \text{SiO}_2(s) + 2\text{H}_2(g)$

b) $\text{SiH}_4(g) + 2\text{N}_2\text{O}(g) \rightarrow \text{SiO}_2(s) + 2\text{H}_2(g) + 2\text{N}_2(g)$

c) $\text{SiH}_2\text{Cl}_2(g) + 2\text{N}_2\text{O}(g) \rightarrow \text{SiO}_2(s) + 2\text{HCl}(g) + 2\text{N}_2(g)$

d) $\text{Si}_2\text{Cl}_6(g) + 2\text{N}_2\text{O}(g) \rightarrow \text{SiO}_2(s) + 3\text{Cl}_2(g) + 2\text{N}_2(g)$

e) $\text{Si}(\text{OC}_2\text{H}_5)_4(g) \rightarrow \text{SiO}_2(s) + 4\text{C}_2\text{H}_4(g) + 2\text{H}_2\text{O}(g)$
• From same precursors and reactants

  - Different films can be deposited

  - By varying

    (i) Ratio of reactants &

    (ii) Deposition conditions
For example:

- Mixture of $\text{Si}_2\text{Cl}_6$ & $\text{N}_2\text{O}$ may deposit
  - Silica films, and
  - Silicon Nitride films

Deposition rates of silica and silicon nitride as functions of the ratio of reactants and deposition conditions.

Reaction kinetics

- Although CVD is nonequilibrium process
  - Controlled by
    (i) Chemical kinetics, &
    (ii) Transport phenomena
- Equilibrium analysis is still useful
  - In understanding the CVD process
• Chemical reaction & phase equilibrium determine:
  - Feasibility of particular process, and
  - Final state attainable

• In a given system
  - Multistep complex reactions are involved
• Fundamental reaction pathways & kinetics
  - Investigated for few industrial important systems

• Complexity of reaction pathways & Kinetics arises:
  - In seemingly simple system, &
  - Deposition process

• Let’s take an example of:
  - Reduction of chlorosilane by hydrogen
• In Si-Cl-H system, at least 8 gaseous species exist:

- $\text{SiCl}_4$, $\text{SiCl}_3\text{H}$, $\text{SiCl}_2\text{H}_2$, $\text{SiClH}_3$,

- $\text{SiH}_4$, $\text{SiCl}_2$, $\text{HCl}$ and $\text{H}_2$

• These 8 species are in equilibrium under:

- Deposition conditions governed by

  (i) Six equations of chemical equilibrium
Composition of gas phase as a function of reactor temperature for a molar ratio of Cl/H=0.01 and a total pressure of 1 atm, calculated using the available thermodynamic data.

Transport Phenomena

• Transport phenomena plays critical role in CVD

• Governs access of film precursors to substrate

• Influences reactions taking place before deposition
  - Degree of desirable &
  - Unwanted gas phase reactions
• Characteristics of CVD chambers have:
  - Complex reactor geometries, &
  - Large thermal gradient characteristics

• Leads to variety of flow structures & affect:
  - Film Thickness
  - Compositional Uniformity, &
  - Impurity Levels
• For most CVD systems

- Characteristic Pressure \( \geq 0.01 \text{ atm} \)

- Mean Free Paths >> Characteristic System Dimension

- Lower gas velocities ~ tens of cm/s

- Reynolds number < 100

- Flows are laminar
• During deposition of CVD Film:
  - Stagnant boundary layer of thickness ($\delta$)
  - Adjacent to growth surface is developed

• In boundary layer,
  - Concentration of growth species decreases
  - From bulk concentration, $P_i$
  - To surface concentration, $P_{io}$ (above growing film)
• Growth species diffuses through boundary
  - Prior to depositing onto growth surface

• In CVD, gas composition is reasonably dilute

• Diffusion flux through boundary layer is:

\[ J_i = \frac{D(P_i - P_{i0})RT}{\delta} \]

(For gas/ growth species)
• ‘D’ is diffusivity in expression & depends on
  - Pressure and Temperature

• ‘D’ can be expressed as:

$$D = D_0 \left( \frac{P_0}{P} \right) \left( \frac{T}{T_0} \right)^n$$
• n is experimentally found to be ~ 1.8

• $D_0$ is value of $D$ measured at
  - Standard temperature $T_0$ (273 K), and
  - Pressure $P_0$ (1 atm)

• $D_0$ depends on gas composition
• For deposition of large area films (above growth surface)
  
  - Depletion of growth species or reactants
  
  - Results in non-uniform film deposition

• To overcome non-uniformity in deposited films
  
  - Various reactor designs are developed
  
  - It improves gas-mass transport (through boundary layer)

E.g. - Low pressure, New Design, Substrate Susceptor
• Several CVD methods & reactors are developed
  - Depending on types of precursors used
  - Deposition conditions applied, and
  - Forms of energy introduced to system

• To activate desired chemical reactions
  - For deposition of solid films on substrates
For example, when precursors used are:

- Metal-organic compounds

- Process is referred as MOCVD (Metalorganic)

When plasma is used to promote chemical reaction

- It is plasma enhanced CVD or PECVD
• There are many other modified CVD methods

Such as,

- LPCVD (low pressure CVD)
- Laser enhanced or assisted CVD, and
- Aerosol-assisted CVD or AACVD
• LPCVD differs from conventional CVD

• Low gas pressure of -0.5 to 1 torr is used

• Low pressure is to enhance
  
  - Mass flux of gaseous reactants & products
  
  - Through boundary layer between

  # Laminar gas stream and substrates
- In PECVD processing,
  - Plasma is sustained within chambers
  - Simultaneous CVD reactions occur
- Typically, the plasma are excited either by
  - RF field (Frequencies: 100 kHz to 40 MHz)
    (Gas pressures: 50 mtorr to 5 torr)
  - Microwave (Frequency ~ 2.45 GHz)
• CVD reactors are generally divided into

- Hot-wall CVD, and

- Cold-wall CVD

Figure depicts a few common setups of CVD reactors.

(1) Horizontal reactor  (2) Vertical reactor  (3) Barrel reactor  (4) Pan-cake reactor

A few common setups of CVD reactors.
• Hot-wall CVD reactors are usually tubular in form
  - Heating in HWCVD is accomplished by
  - Surrounding reactor with resistance element

• In typical cold-wall CVD reactors,
  - Substrates are directly heated
  - Inductively by graphite susceptors
  - Chamber walls are air or water-cooled
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