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

$SiH_4(g) \rightarrow Si(s) + 2H_2(g)$ at 650°C

$Ni(CO)_4(g) \rightarrow Ni(s) + 4CO(g)$ at 180°C

(B) Reduction

$SiCl_4(g) + 2H_2(g) \rightarrow Si(s) + 4HCl(g)$ at 1200°C

$WF_6(g) + 3H_2(g) \rightarrow W(s) + 6HF(g)$ at 300°C

(C) Oxidation

$$SiH_4(g) + O_2(g) \rightarrow SiO_2(s) + 2H_2(g) \text{ at } 450°C$$

$$4PH_3(g) + 5O_2(g) \rightarrow 2P_2O_5(s) + 6H_2(g) \text{ at } 450°C$$

(D) Compound Formation

$$SiCl_4(g) + CH_4(g) \rightarrow SiC(s) + 4HCl(g) \text{ at } 1400°C$$

$$TiCl_4(g) + CH_4(g) \rightarrow TiC(s) + 4HCl(g) \text{ at } 1000°C$$

(E) Disproportionation

$2GeI_2(g) \rightarrow Ge(s) + GeI_4(g)$ at 300°C

(F) Reversible Transfer

$As_4(g) + As_2(g) + 6GaCl(g) + 3H_2(g)$

$\rightarrow 6GaAs(s) + 6HCl(g)$ at 750°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) $SiH_4(g) + O_2(g) \rightarrow SiO_2(s) + 2H_2(g)$

b) $SiH_4(g) + 2N_2O(g) \rightarrow SiO_2(s) + 2H_2(g) + 2N_2(g)$

c) $SiH_2Cl_2(g) + 2N_2O(g) \rightarrow SiO_2(s) + 2HCl(g) + 2N_2(g)$

d) $Si_2Cl_6(g) + 2N_2O(g) \rightarrow SiO_2(s) + 3Cl_2(g) + 2N_2(g)$

e) $Si(OC_2H_5)_4(g) \rightarrow SiO_2(s) + 4C_2H_4(g) + 2H_2O(g)$

- From same precursors and reactants

  - Different films can be deposited

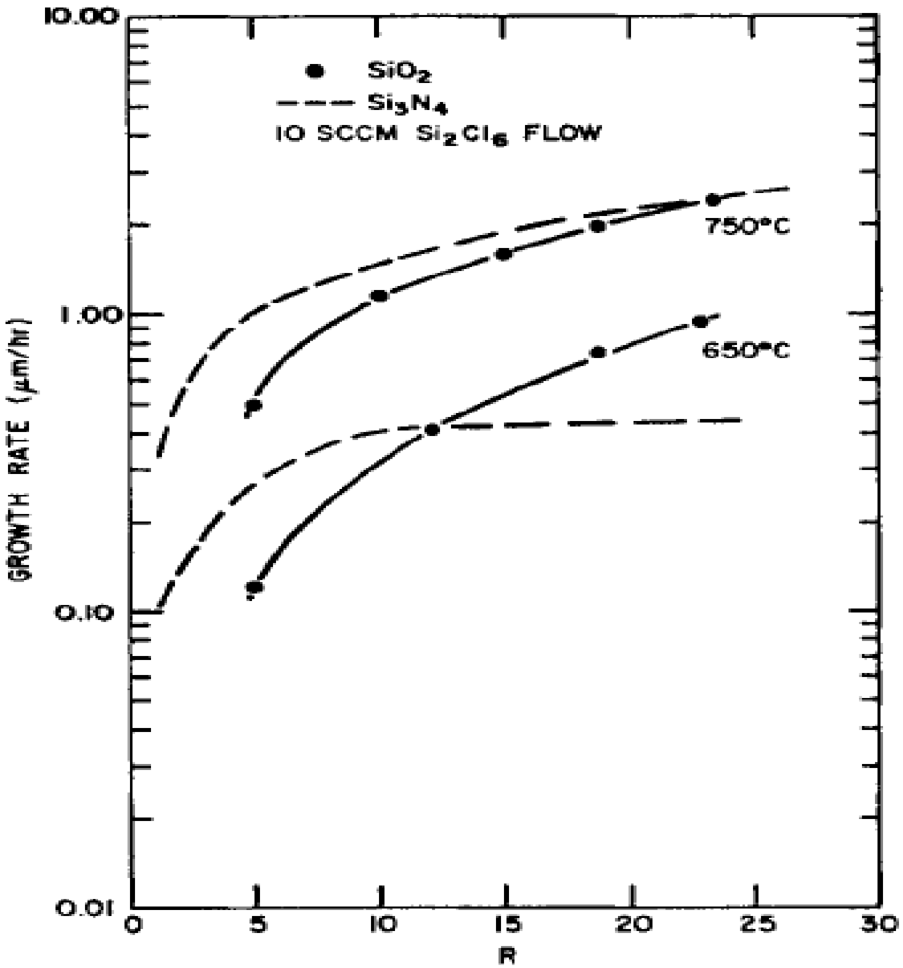
  - By varying

    (i) Ratio of reactants &

    (ii) Deposition conditions

For example:

- Mixture of Si_2Cl_6 & N_20 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.

Ref: R.C. Taylor and B.A. Scott, J. Electrochem. Soc., 136(1989)2382.

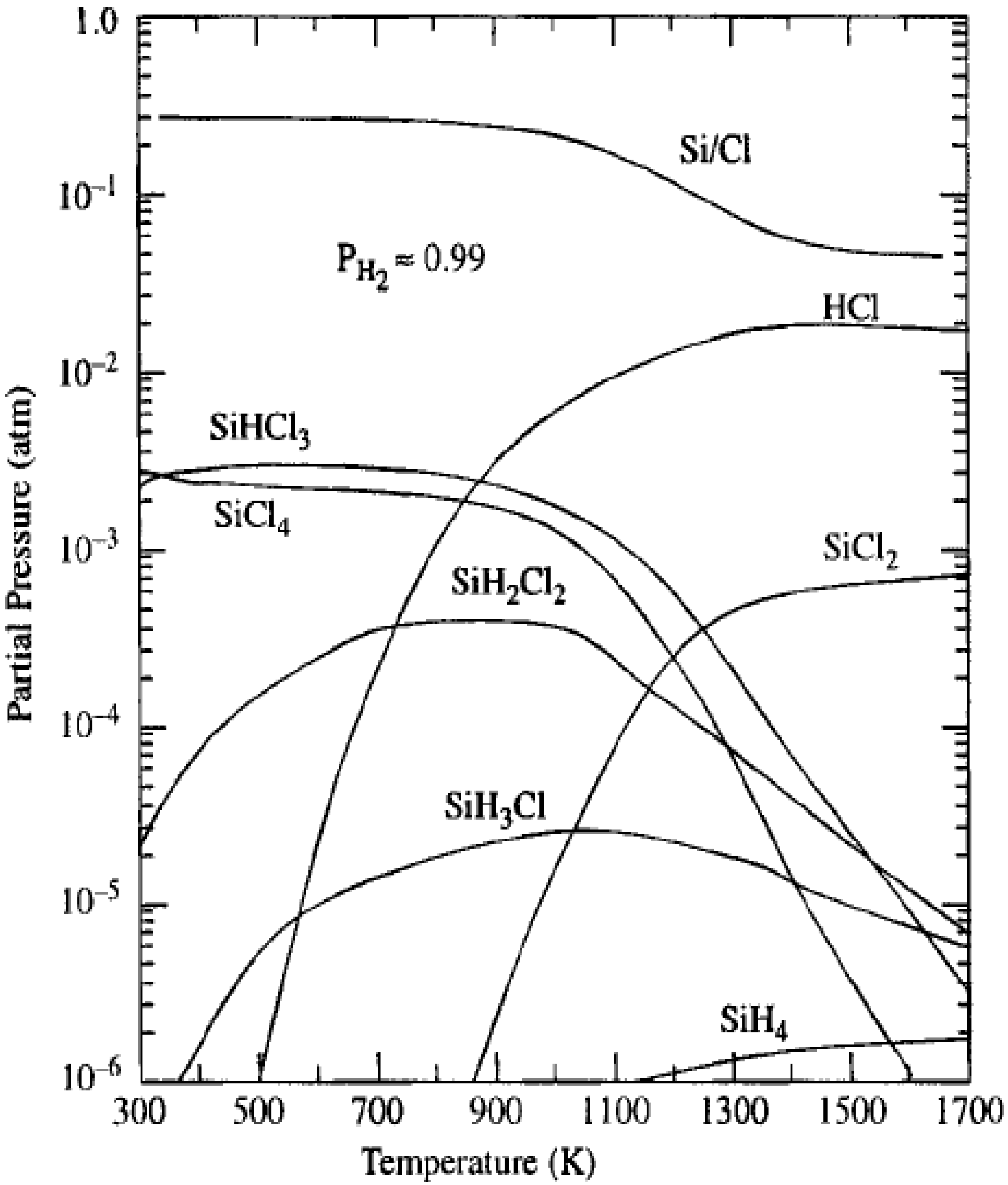
Reaction kinetics

- 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:
  - $SiCl_4$, $SiCl_3H$, $SiCl_2H_2$, $SiClH_3$,
  - SiH_4, $SiCl_2$, HCl and 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.

Ref: E.Sirtl, L.P.Hunt, and D.H.Sawyer, J. Electrochem. Soc., 121(1974)919.

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 ≥ 0.01 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 (δ)
  - Adjacent to growth surface is developed
- In boundary layer,
  - Concentration of growth species decreases
  - From bulk concentration, *Pi*
  - To surface concentration, *Pio* (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:

$$J_i = \frac{D(P_i - P_{io})RT}{\delta}$$

(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_o is value of D measured at
    - Standard temperature T_o (273 K), and
    - Pressure P_o (1 atm)
- D_o 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)

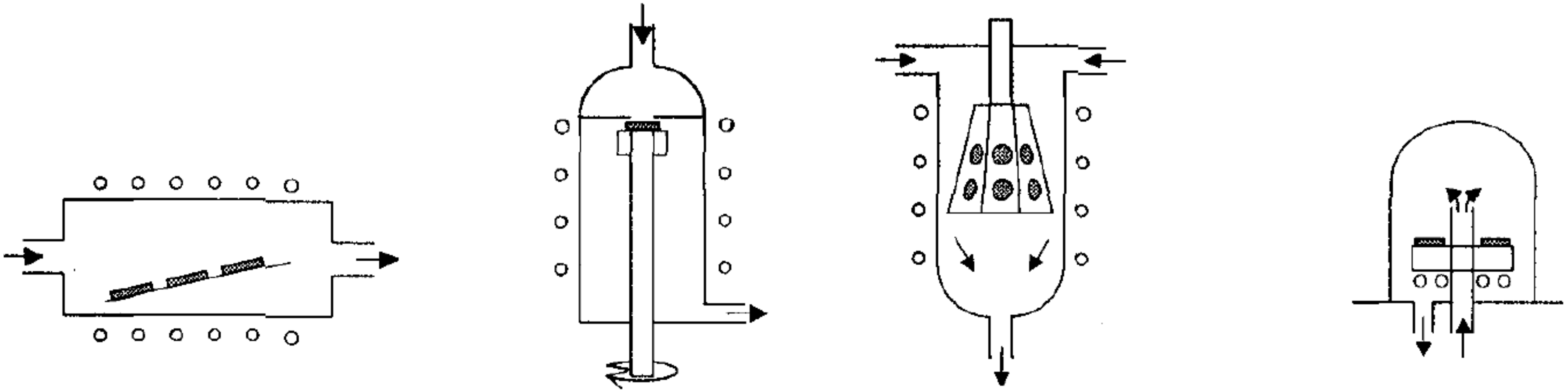
    - Microwave (Frequency ~ 2.45 GHz)

- 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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