Chemical Vapor Deposition (cont.)
CVD Reactor Notes

• The kinetics of your reaction mostly determines the choice of the reactor type.

• Mass transport limited growth (high T):
  – Should be able to control gas flow and pressure to get uniform films

• Reaction rate limited growth (low T, low P):
  – Should be able to control the temperature profile for uniform films
CVD Reactor Types by Architecture

• Tube reactors
• Showerhead reactors
• High-density plasma reactors
• Linear injection reactors
Tube Reactors

- Hot wall design (the reactor walls are heated).
- Can be horizontal or vertical.
- Batch processing of wafers
- Good radial uniformity of films
- Axial uniformity more suspect
- Need to slow down deposition rates for axial uniformity.
Showerhead Reactors

- Cold wall design (only substrate is heated)
- Better suited for plasma enhanced processing.
- Generally a single wafer design.
- Good heater design is needed for radial uniformity.
CVD Reactor Types by Process

- APCVD – Atmospheric Pressure CVD
- LPCVD – Low Pressure CVD
- MOCVD – Metalorganic CVD
- PHCVD – Photon (Laser) Induced CVD
- PECVD – Plasma Enhanced CVD
Thermal CVD Processes

• Heat energy is supplied to activate the required gas and gas-solid phase reactions.
• There are many possible classifications to the thermal CVD processes:
  – High or low temperature
  – Atmospheric or low pressure
  – Cold or hot wall
  – Closed or open.
• Still all of them have to be able to,
  – deliver the reactant gases to the reactor,
  – supply heat to the substrates for efficient deposition
  – and remove the by-products.
Atmospheric Pressure CVD

• High Temperature APCVD
  – Used to deposit epitaxial Si and compound films (cold wall reactors) or hard metallurgical coatings like TiC and TiN (hot wall reactors).

**Cold Wall Reactor**
• wafers tilted for uniform deposition

**Hot Wall Reactor**
Atmospheric Pressure CVD

- Low Temperature APCVD
  - Many insulating film layers (SiO$_2$, BPSG glasses) need to be deposited at low temperatures.
APCVD Issues

- Wafer throughput is low due to low deposition rate.
- Film thickness uniformity can be an issue.
- Step coverage is not very good.
- Contamination is a problem and maintaining stochiometry can be hard.
- Large number of pinhole defects can occur.
Low Pressure CVD

• Classify by gas pressure:
  – For 100 torr > P > 1 torr, we have reduced pressure CVD (RPCVD)
  – For 10 mtorr > P > 1 mtorr, we have LPCVD
  – At UHV (~$10^{-7}$ torr), we have UHV/CVD.
• Higher gas concentrations to compensate for lower pressure.
• Higher diffusivity of gas to the substrate
• Often reaction rate limited growth
• Due to lower pressures, there are fewer defects.
• Better step coverage, better film uniformity.
LPCVD Reactors

- Reaction rate limited growth enables close packed stacking of wafers in LPCVD chambers, resulting in high wafer throughput.
- Can be “hot wall” or “cold wall” reactors
- Most commercial LPCVD reactors are hot walled.
- Hot wall reactors have a more uniform temperature distribution but the surface of the reactor walls can also get coated. This limits the reactor to one species. Used more for polycrystalline films.
- In cold wall reactors, the reaction rate is reduced but film quality can be better controlled. Better for epitaxial films.
LPCVD Summary

• Fewer defects
• No need for a carrier gas (not transport limited)
• Slow growth rate
• Good conformation (step coverage)
• High temperature dependence
Metalorganic CVD (MOCVD)

- Use organometallic source gasses.
- eg: $(\text{CH}_3)_3\text{Ga}$ . . . . tri-methyl Gallium
- Reactants are volatile at relatively low temperatures.
- Can grow high quality epitaxial films at nanometer scale.
- Both the reactants and the byproducts can be hazardous.
Photon Enhanced CVD (PHCVD)

- Use a laser to enhance surface reactions
- Two main processes are involved:
  - pyrolytic
    - heats substrate to enhance reactions
  - photolytic
    - gas phase dissociation of molecules to enhance reactivity
    - typically use UV radiation

Fig. 1. Schematic diagram of the L-CVD deposition apparatus.

Plasma Enhanced CVD Processes

- Create a plasma (RF or DC) in the vicinity of the substrate.
- As in sputtering, the energetic ions impart their energy and momentum on the reactant gas molecules and atoms.
- The energy transfer breaks up the molecules and aids the chemical reactions.
Plasma Enhanced CVD (PECVD)

• The “helping hand” of the plasma allows for lower temperatures and pressures and improves film quality.
• For example, TiC would not normally form below 1200 °C (from GFE consideration) but with PECVD, it is possible to deposit it at 700 °C.
• The lower temperatures are especially useful when depositing metal contact layers (eg. Al) between dielectric (insulating) layers (eg. SiO$_2$).
• The higher temperatures of plain LPCVD would melt the metal and the alternate layers would interact.
• The imparted momentum allows for better step coverage.
PECVD

• Compared to sputtering, the pressures are higher (50 mtorr – 5 torr), meaning the ions are less energetic when they hit the substrate (more collisions to lose energy).
• This reduces the sputtering effects on the substrate.
• For insulating films, again, RF plasma can be used to minimize coating.
PECVD Reactors

• Reinberg type reactor (direct)
  – Reactants, by-products, substrates and plasma are in the same space.
  – Parallel plate design
  – Rotating substrates
  – Capacitively coupled RF plasma

• Downstream reactor (indirect)
  – Plasma is generated in a separate chamber and is pumped in to the deposition chamber
  – Allows better control of film quality, purity and stochiometry
Structure of CVD Grown Films

- The main parameters affecting film structure are substrate temperature and vapor supersaturation.
  - Temperature determines growth rate.
  - Supersaturation determines nucleation rate.
- Together they determine whether epitaxial or amorphous films, whiskers, platelets, polycrystals, etc. are produced.
- In general, single crystal growth is favored by low supersaturation and high substrate temperatures, and amorphous films are favored by the opposite situation.
Carbon Nanotubes

- Carbon nanotubes are tubular structures of carbon, typically several nanometers in diameter and hundreds to thousands of nanometers in length.
- They can be single or multiwalled.
- Can have a wide range of electrical, mechanical and optical properties.
CVD Growth of Carbon Nanotubes

- A hydrocarbon gas is passed over a catalyst in a high temperature oven.
- The catalyst (often transition-metal nanoparticles on alumina) allows the dissociation of the hydrocarbon.
- The carbon then dissolves and saturates the nanoparticles.
- Upon precipitation from the catalyst, carbon atoms form nanotubes (energetically favored over graphite sheet formation).
- The chamber is cooled to room temperature and the tubes are collected.
- The choice of the hydrocarbon, the catalyst and the temperature determine the nature of the nanotubes.
CNT Growth Details

• MWCNT
  – Ethylene or acetylene as the hydrocarbon
  – Temperature: 550 °C – 700 °C
  – Nickel or Cobalt nanoparticles as catalyst

• SWCNT
  – Methane as the hydrocarbon
  – Temperature: 850 °C – 1000 °C
  – Nickel, Cobalt or Iron nanoparticles as catalyst
Selective Deposition of Films

- While CVD is mainly thought of as a blanket deposition process, creative use of chemistry can allow for selective deposition.
- Suppose we have neighboring Si and SiO₂ regions and we would like to deposit tungsten on the Si but not the oxide. The usual reduction reaction is not useful since it will indiscriminately cover both species.
- However, if the reducing agent is solid silicon, then the reaction will take place only on the silicon and not the oxide.
- The reaction will continue until all the silicon is covered.

\[
WF_6(g) + 3H_2 \rightarrow W(s) + 6HF(g) \quad \text{usual tungsten reduction}
\]

\[
2WF_6(g) + 3Si(s) \rightarrow 2W(s) + 3SiF_4(g) \quad \text{tungsten reduction with silicon}
\]
Safety

• The precursors and by-products in CVD processes are mostly toxic, pyrophoric, corrosive and flammable.
• Silane can ignite upon contact with air and can explode in areas with stagnant air. Therefore silane cylinders are generally stored outside the building in concrete bunkers.
• Corrosion of gas handling components (valves, regulators, piping) is very common.
• Exhaust systems contain abrasive particulates and corrosive species.