Chemical Vapor Deposition (cont.)

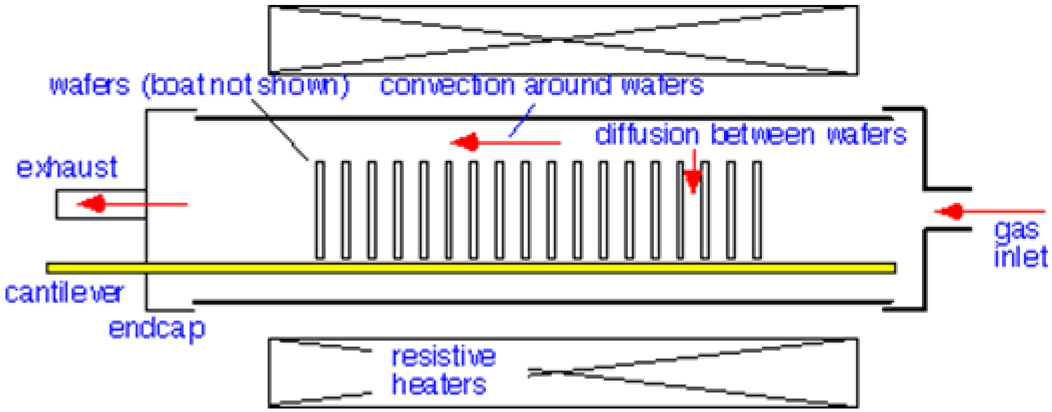
CVD Reactor Notes

- 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

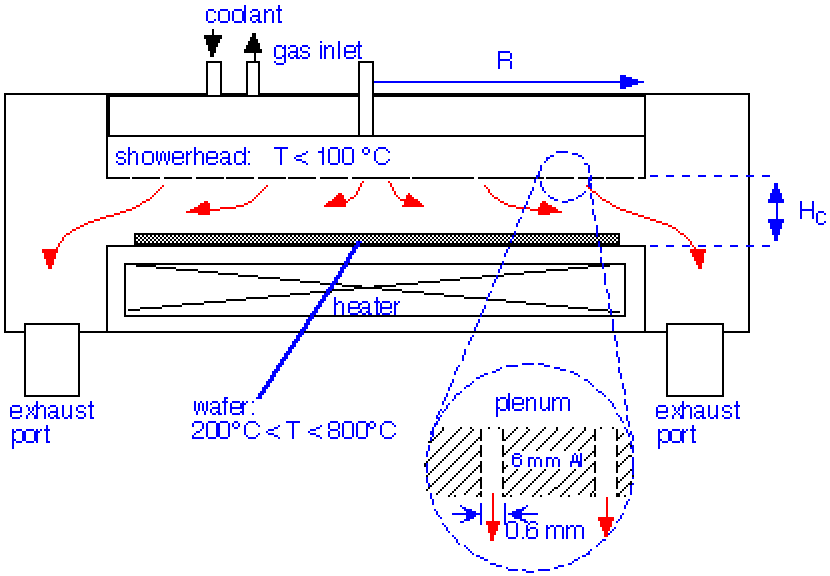
Tube Reactors



- 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

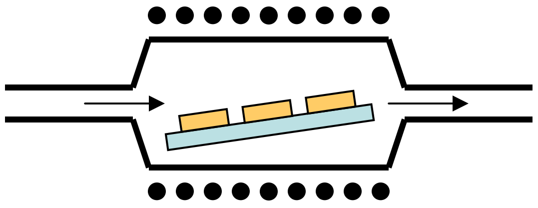
- APCVD – Atmospheric Pressure CVD
- LPCVD – Low Pressure CVD
- MOCVD – Metalorganic CVD
- PHCVD – Photon (Laser) Induced CVD
- PECVD – Plasma Enhanced CVD

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.

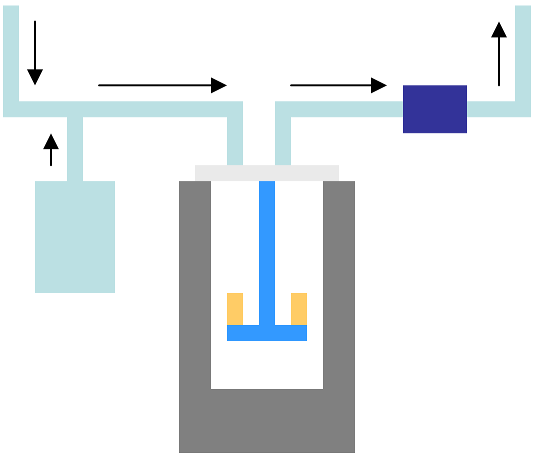
Atmospheric Pressure CVD

- 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

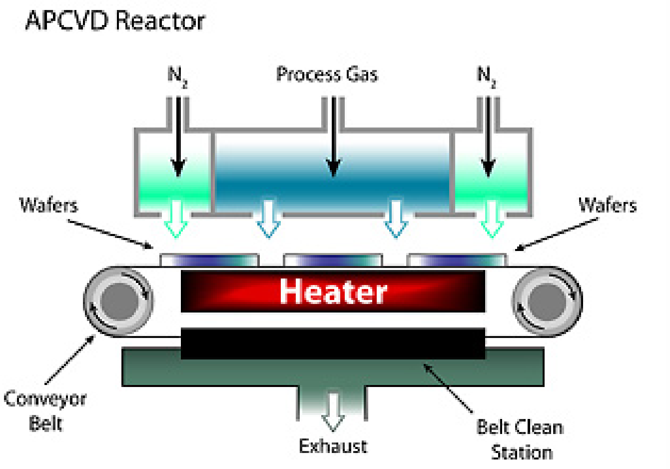
- wafers tilted for uniform deposition



Hot Wall Reactor

Atmospheric Pressure CVD

- Low Temperature APCVD
  - – Many insulating film layers (SiO_2, BPSG glasses) need to be deposited at low temperatures.



Conveyor Belt Reactor

APCVD Issues

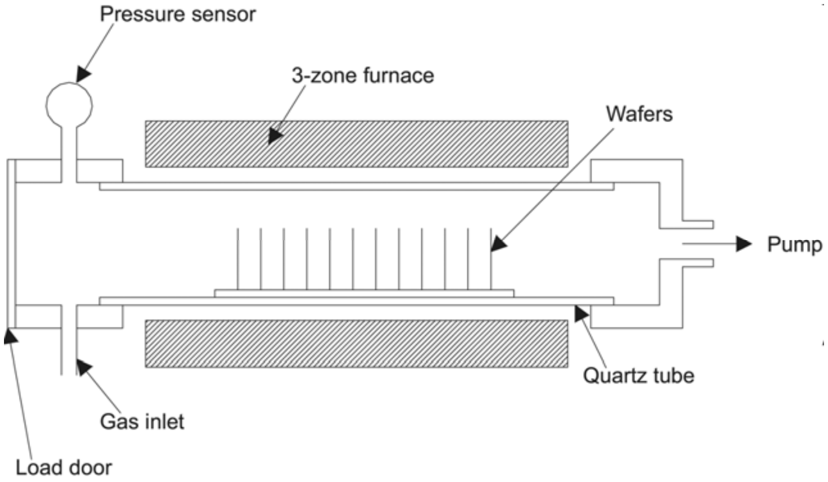
- Wafer throughput is low due to low deposition rate.
- Film thickness uniformity can be an issue.
- Step coverage is not very good.
- Contamination is a problem and maintaining stochiometry can be hard.
- Large number of pinhole defects can occur.

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.



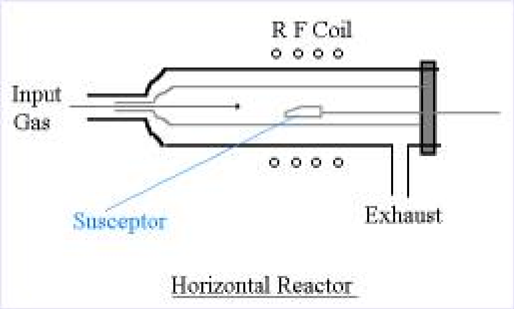
Hot wall reactor

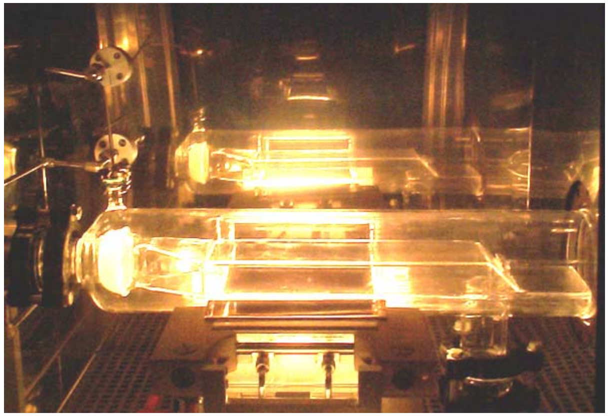
LPCVD Summary

- 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: $(CH_3)_3Ga$ . . . . 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

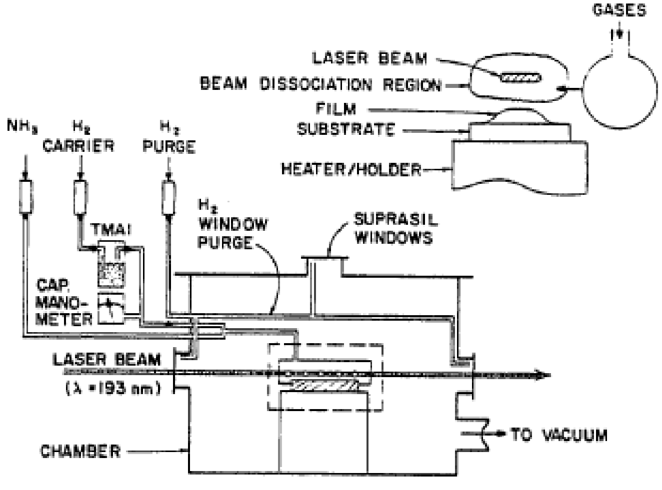
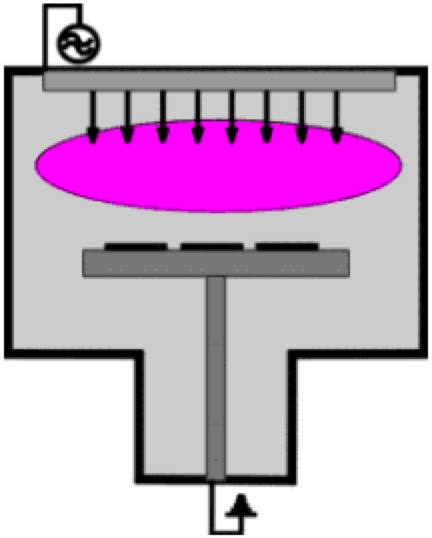


Fig. 1. Schematic diagram of the L-CVD deposition apparatus.

Appl. Opt., v25, pp 1311-1317, 1986

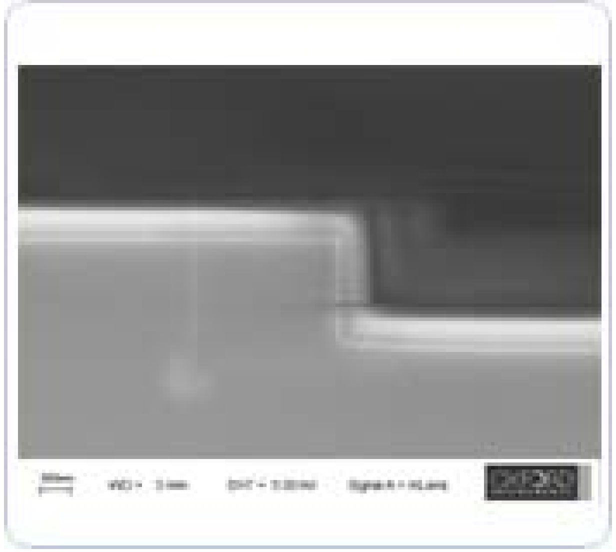
Plasma Enhanced CVD Processes

- 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.



Step coverage in PECVD

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

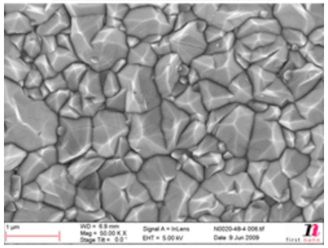
- Reinberg type reactor (direct)
  - Reactants, by-products, substrates and plasma are in the same space.
  - Parallel plate design
  - Rotating substrates
  - Capacitively coupled RF plasma

- 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

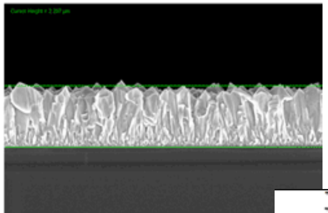
Structure of CVD Grown Films

- 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.

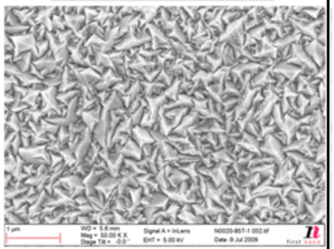
Top View of APCVD F:ZnO



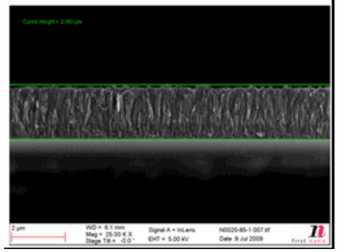
Cross-section View of APCVD F:ZnO



Top View of LPCVD B:ZnO

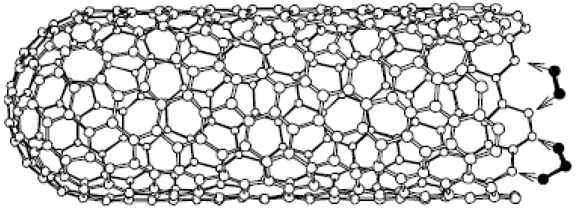


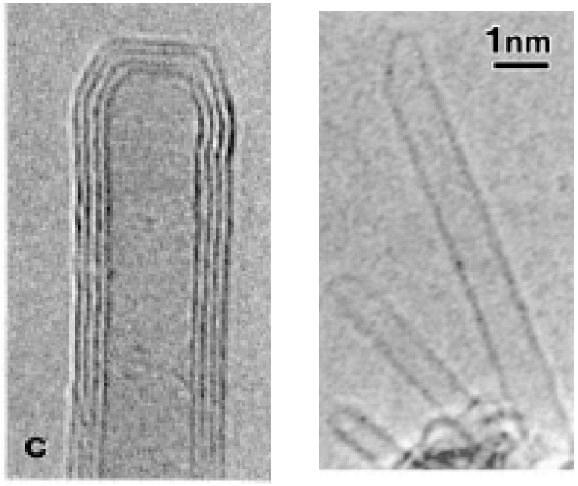
Cross-section View of LPCVD B:ZnO



Carbon Nanotubes

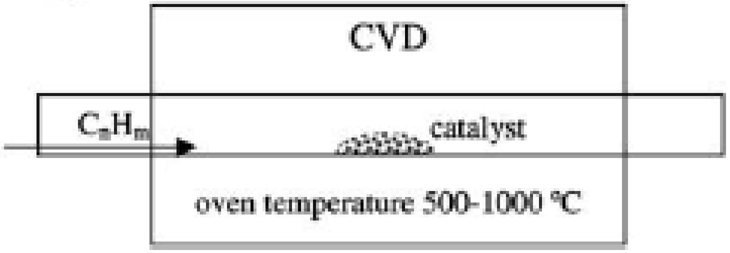
- Carbon nanotubes are tubular structures of carbon, typically several nanometers in diameter and hundreds to thousands of nanometers in length.
- They can be single or multiwalled.
- Can have a wide range of electrical, mechanical and optical properties.

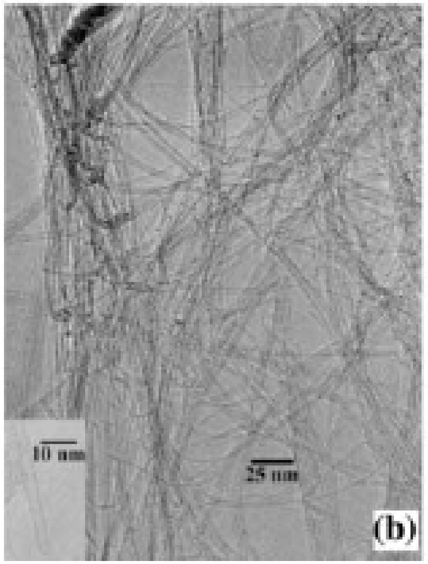




CVD Growth of Carbon Nanotubes

- 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 SiO_2 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.

$WF_6(g) + 3H_2 \rightarrow W(s) + 6HF(g)$ usual tungsten reduction

$2WF_6(g) + 3Si(s) \rightarrow 2W(s) + 3SiF_4(g)$ 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.