Course name: Growth and Characterization of Nanoelectronic Materials (EE728)

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CVD Kinetics

The flux across the boundary layer at steady state

$$F_1 = -D_G \frac{\partial C}{\partial x} = \frac{D_G}{\delta_S} (C_G - C_S)$$
$$h_G = \frac{D_G}{\delta_S}$$

The Position of boundary layer as a function of x

$$\delta_{S}(x) = \left(\frac{\mu x}{\rho U}\right)^{1/2}$$

ρ=gas density, μ=gas viscosity,

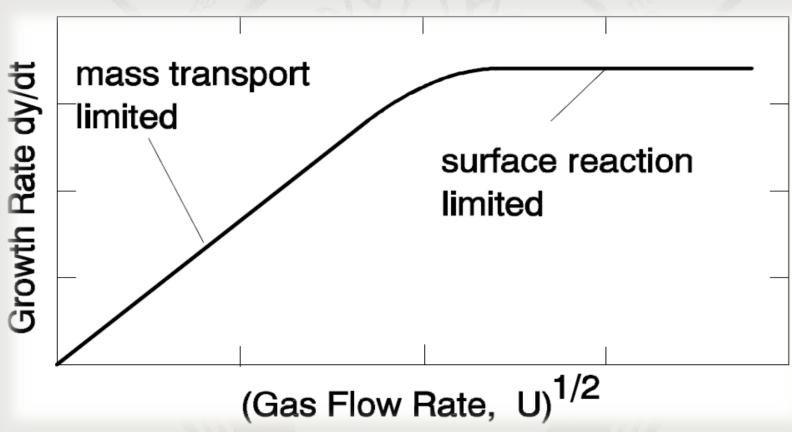
- As x increases , δ_S increases along the susceptor, then h_G decreases,
- Deposition rate would decrease going from the front of the susceptor to the back

CVD Kinetics

- Source gas depletion occurs along the length of the susceptor.
- ➤ The conc. of reactant species decreases with distance along the susceptor.
- ➤ Growth rate is proportional to the partial pressure of the reacting species, the growth rate will decrease along the length of the susceptor.
- Growth rate decrease due to :
- > increasing boundary layer : Mass Transfer regime
- Reactant depletion : Mass Transfer & Surface reaction controlled regime

CVD growth kinetic – Gas phase mass transfer

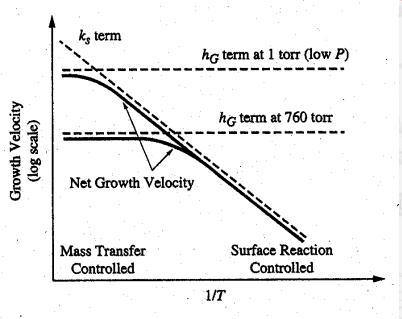




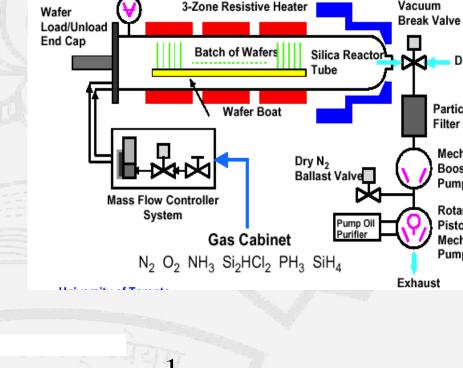
CVD Kinetics:

Example: Low Pressure Chemical vapor deposition

(LPCVD)



Recall that
$$t = \frac{F}{N} = \frac{k_S h_G}{k_S + h_G} \frac{C_T}{N}$$



Horizontal LPCVD Reactor

Water-Cooled End

Particulate

Mechanical

Booster

Pump

Rotary

Piston

Pump

Mechanical

Filter

Cap Assembly

and
$$h_G = \frac{D_G}{\delta}$$

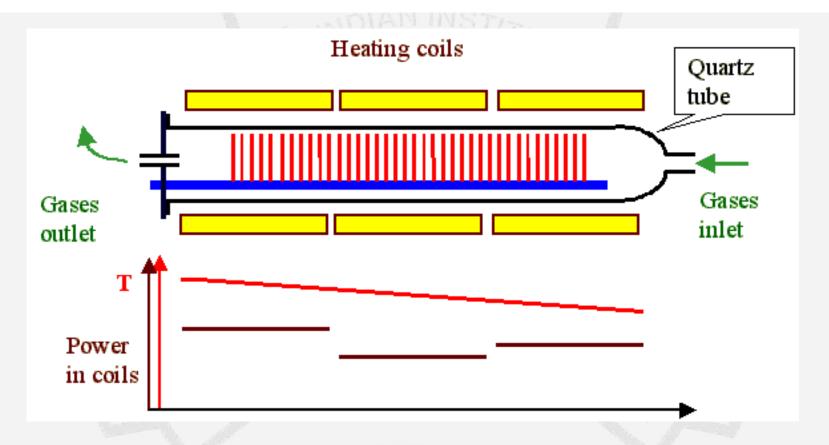
The key new point is

$$D_G \propto rac{1}{P_{total}}$$

Pressure

Gauge

Gas depletion in LPCVD reactor

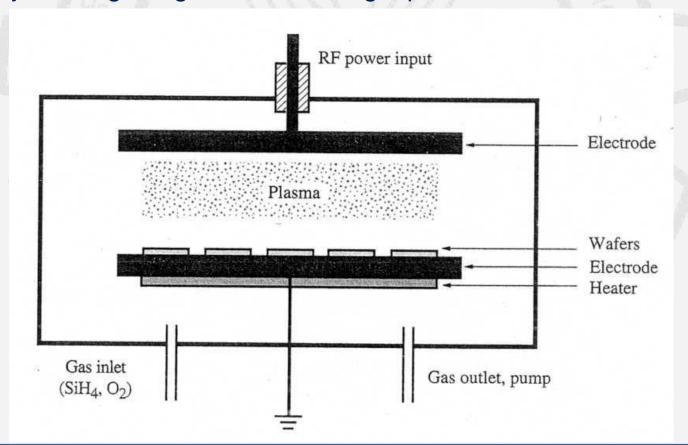


In the surface reaction limited regime T is critical (\nearrow 1°C). Ramping T compensates depletion.

Plasma Enhanced CVD (PECVD) Plasma Assisted CVD (PACVD)

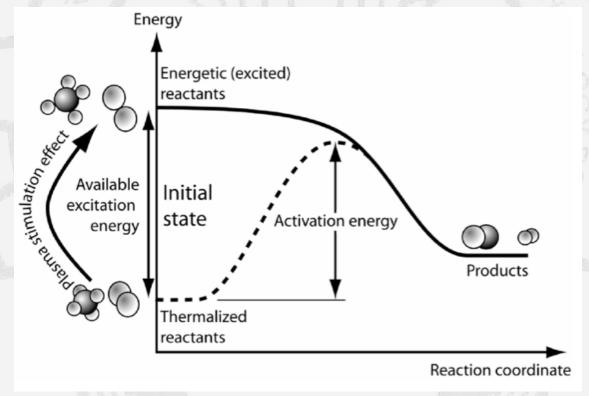
Plasma enhanced CVD system (PECVD)

As the thermal budget gets more and more constrained while more and more layers need to be added for multi-layer metallization, we want to come down with the temperature for the oxide (or other) CVD processes. One way for doing this is to supply the *necessary energy for the chemical reaction* by ionizing the gas, thus forming a plasma.



Plasma Enhanced CVD

- > Energy is required for the CVD reactions to happen
- In thermal CVD the energy is supplied by thermal means (Heat)
- > The reactant species can be excited by a variety of means
- The substrate temperature can be significantly low

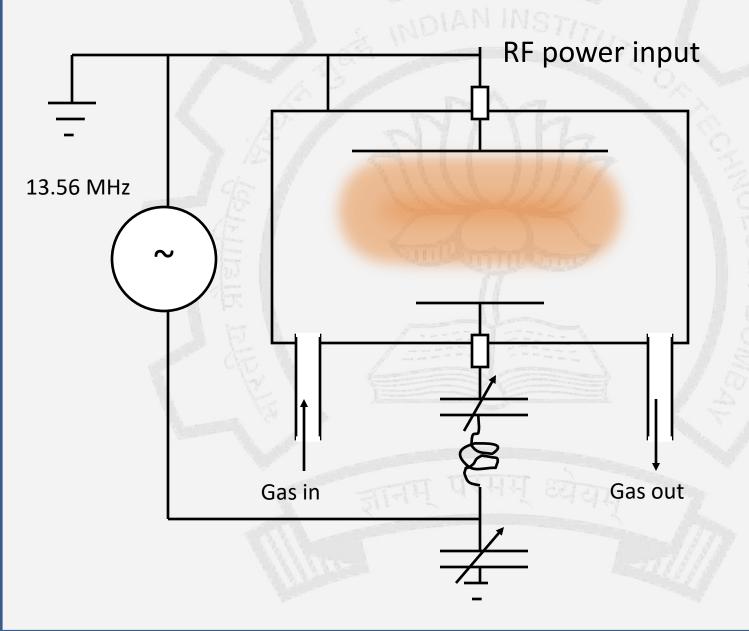


Angus Rockett, "Material Science of Semiconductors", Springer Verlag, 2008

Plasma Enhanced CVD (2)

- Species in excited state in a plasma can react at much lower temperature than ground state molecules
 - ➤ Lower temperature of deposition. E.g.: PECVD Si₃N₄ can be deposited at a substrate temperature of even 30C, whereas thermal CVD requires ~ 750C.
 - Compatible with metal layers used for interconnects
 - Reaction limited by mass transport
- lons in the plasma may be used for sputtering, leading to a combination of deposition and physical etch
 - Used for gap filling applications like STI and pre-metal dielectric gap fills
 - Etching can be used for cleaning the wafer before deposition and for chamber cleaning between depositions
- Variety of species not available in a thermal reactor may be present
 - Larger variety of reaction pathways
 - ➤ E.g. Si₃N₄ can be deposited by reacting SiH₄ and N₂ in PECVD. Thermal CVD nitride requires NH₃.

RF Plasma



RF Plasma (2)

- ☐ Steady state
 - ➤ Energy is transferred to the plasma by capacitive coupling, the electrons in the plasma would oscillate with the applied RF signal

- ➤ Ions at the edges of the sheaths can be accelerated towards the electrodes
- > Free radicals can diffuse to the electrodes from the plasma

RF Plasma (3)

Electrons – impact reactions in the plasma

Excitation

$$e + X_2 \rightarrow X_2^* + e$$

Dissociation

$$e + X_2 \rightarrow 2X + e$$

Ionization

$$e + X_2 \rightarrow X_2^+ + 2e$$

Dissociative ionization

$$e + X_2 \rightarrow X^+ + X + 2e$$

Result: free radicals, ions and electrons

Hess and Graves, Chapter 7 in Chemical Vapor Deposition Principles and Applications, edited by Hitchman and Jensen, Academic Press, 1993

PECVD Applications

☐ Low temperature of deposition

- ➤ Si₃N₄, a-Si films deposited by PECVD may contain more hydrogen than LPCVD films
 - Passivation of layers in crystalline Si solar cells
 - Lower density of defects in a-Si:H than in a-Si leading to thin film solar cells applications
 - Stress control => mobility enhancement in CMOS FETs
- Low thermal budget => preferred thin film deposition scheme for backend of line VLSI processing
- **❖** Possibility to combine reactive ion etching and deposition
 - √ Isolation layers in VLSI technology => Gap fill

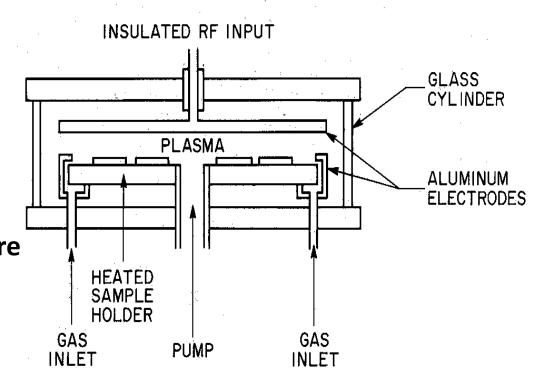
Advantages of PECVD: Comparison with CVD

Film	Precursors	Thermal deposition	Plasma- enhanced
Silicon nitride	SiH4 or SiH ₂ Cl ₂ and NH3	750°C	200-500 °C
Silicon dioxide	SiH ₄ and O ₂ [or often N ₂ O]	350-550 °C	200-400 °C
	Tetraethoxysilane (TEOS) and O ₂	700-900 °C	300-500 °C
Amorphous silicon	SiH ₄	550-650 °C	200-400 °C

[✓] Deposition at much lower temperatures and pressures than that would be required for thermal CVD.

PECVD Reactor configurations

- ▶ 50 kHz ~ 13.56 MHz power source
- Vacuum: 0.1∼5 torr
- Advantages:
 - Low deposition temperature
 - Low power source
- Disadvantages:
 - Limited capacity
 - Individual wafer loading
 - Easily contaminated



Processes of Interest in PECVD

- Transport of the ionized species and radicals through the plasma
 Reactions in the plasma are undesirable as this can cause particle
 - Reactions in the plasma are undesirable as this can cause particle formation and deposition on the wafer
- Fast moving particles impinging the substrate from the plasma
 - Ions and radicals => deposition
 - Electrons
 - Sputtering gas (Ar, Xe,.....)

Modification of deposited film

Limited capacity:

PECVD systems require wafers to lie flat on the bottom wafer. Only one wafer side can be coated at a time unlike LPCVD (wafers loaded vertically). PECVD can coat 1~4 wafers at one time whereas LPCVD can coat up to 25 wafers

Four Basic CVD Reactors

1. Atmospheric Pressure CVD (APCVD)

Advantages: High deposition rates, simple, high throughput Disadvantages: Poor uniformity, purity is less than LPCVD Used mainly for thick oxides.

2. Low Pressure CVD (LPCVD at ~0.2 to 20 torr)

Advantages: Excellent uniformity, purity

Disadvantages: Lower (but reasonable) deposition rates than APCVD Used for polysilicon deposition, dielectric layer deposition, and doped dielectric deposition.

3. Plasma Enhance CVD

Plasmas are used to force reactions that would not be possible at low temperature.

Advantages.: Uses low temperatures necessary for back end processing.

Disadvantages: Plasma damage typically results.

Used for dielectrics coatings.

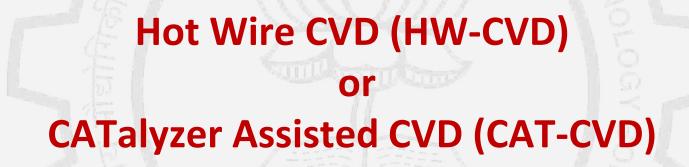
4. Metal Organic CVD (MOCVD)

Advantages.: Highly flexible—> can deposit semiconductors, metals, dielectrics Disadvantages: *HIGHLY TOXIC!*, Very expensive source material. Environmental disposal costs are high.

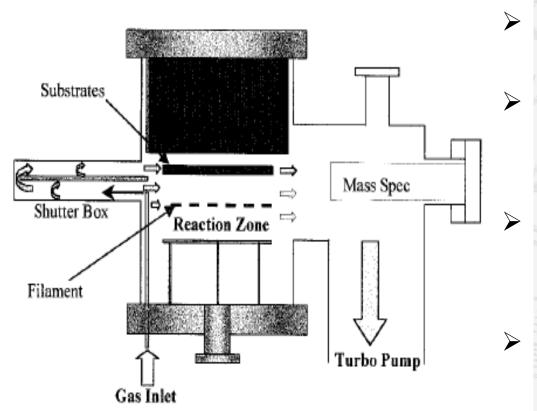
Uses: Dominates low cost optical (but not electronic) III-V technology, some metalization processes (W plugs and Cu)

Glow Discharge in ICP-CVD System





HW-CVD/CAT-CVD Reactor

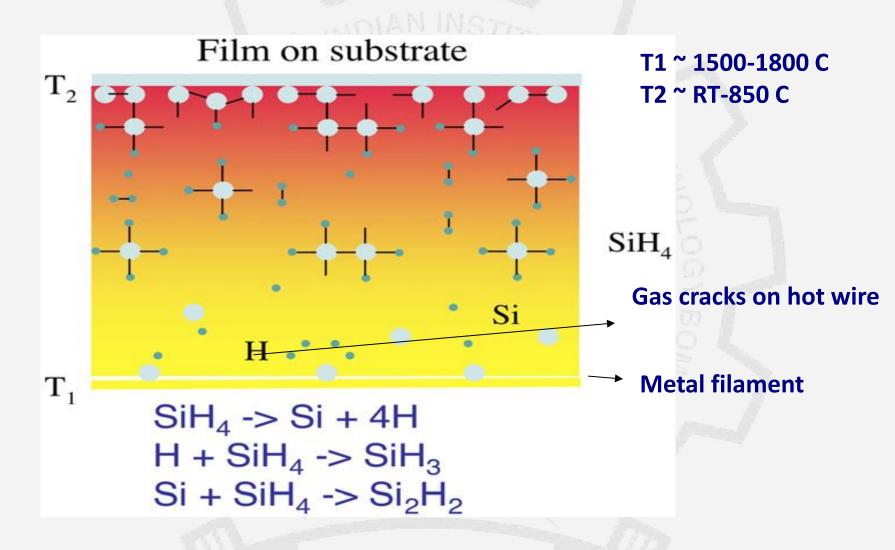


Heated filament typically Ta or W, mounted in centre of reactor W or Ta acts as catalysts for precursor decomposition and hence the name CAT-CVD

- Substrate heated by resistive coil heaters, film quality depends on substrate temperature
- Shutter cuts off the substrate from reactant supply to block deposition

Pant, et. al., Ind. Eng. Chem. Res., Vol. 40, No. 5, 2001

HW-CVD: a-Si

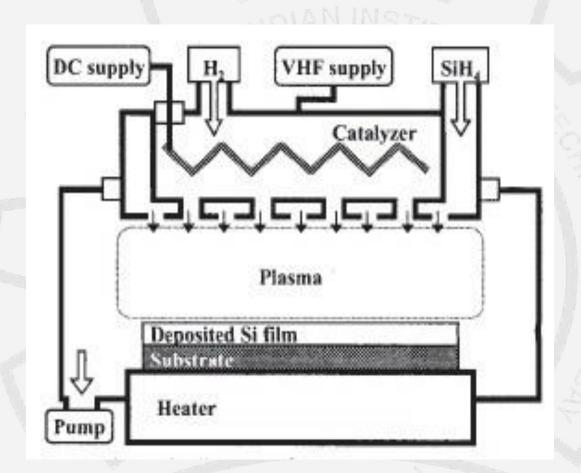


Q. Wang, Thin Solid Films 517 (2009).

HW-CVD for a-Si:H

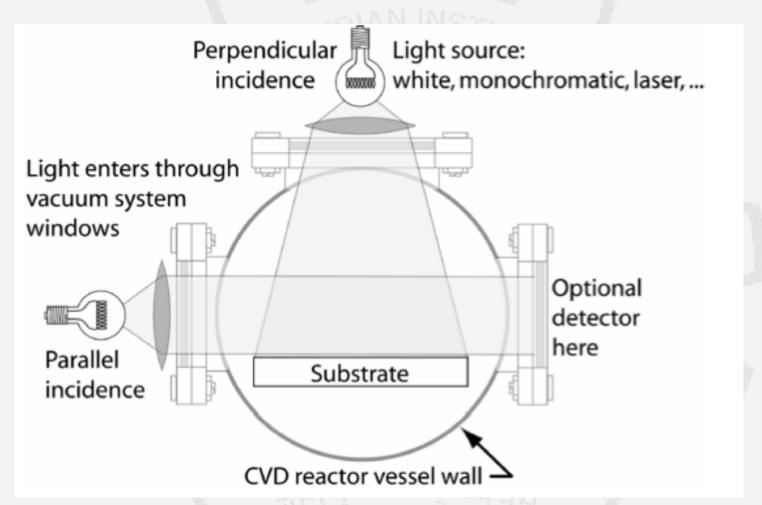
- Primary radical species are Si and H
- React with Silane to give secondary radical species
- > Si release decreases as temperature of filament is reduced
- Deposition chemistry, growth rate can be tailored by filament temperature, Silane pressure and hot-wire surface area
- ➤ Filaments last ~10 hours

Plasma Enhanced HW-CVD



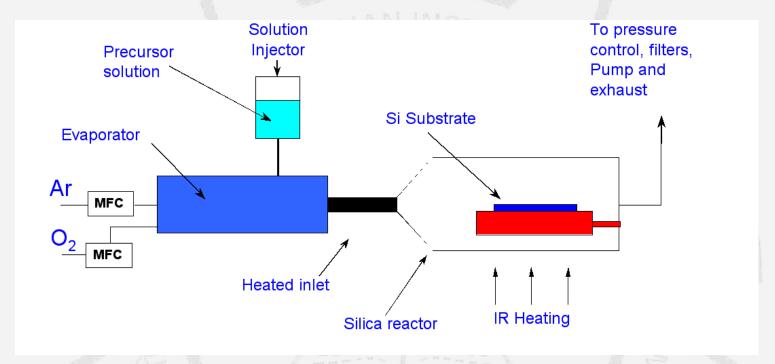
M. Komoda et al., 3rd World, Conference on Photovoltaic Energy Conversion, 2003

Light Induced CVD



John E. Mahan, "Physical Vapor Deposition of Thin Films", John Wiley and Sons, 2000

MOCVD: Metal Organic Chemical Vapor Deposition



In MOCVD ultra pure gases are injected into a reactor and finely dosed to deposit a very thin layer of atoms onto a semiconductor wafer. Surface reaction of organic compounds or metalorganics and hydrides containing the required chemical elements creates conditions for crystalline growth - epitaxy of materials and compound semiconductors.

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