Chemical Vapor Deposition (CVD)

More conformal deposition vs. PVD

(∵ higher temp has higher surface diffusion)

Shown here is 100% conformal deposition
(a) \(SiO_2\) gas \(\rightarrow\) solid

\[SiH_4 + O_2 \rightarrow SiO_2 + 2H_2\uparrow\]

\(350^\circ \text{C}-500^\circ \text{C}\)

(b) PSG: phospho silicate glass. \([P_2O_5 + SiO_2]\)

\[4PH_3 + 5O_2 \rightarrow 2P_2O_5 + 6H_2\]

\[SiH_4 + O_2 \rightarrow SiO_2 + 2H_2\uparrow\]

\(350^\circ \text{C}-500^\circ \text{C}\)

(c) TEOS: tetraethylene orthosilicate.

\[Si(OC_2H_5)_4 \rightarrow SiO_2 + C_XH_YO_Z\uparrow\]
\[(d) \quad \text{Si}_3 \text{N}_4 \quad 3 \text{SiH}_4 + \text{NH}_3 \rightarrow \text{Si}_3 \text{N}_4 + 12 \text{H}_2 \]

\[(e) \quad \text{Poly} - \text{Si} \quad \text{SiH}_4 \rightarrow 600^\circ_C \rightarrow \text{Si} + 2\text{H}_2 \]

\[(f) \quad \text{W} \quad \text{WF}_6 + 3\text{H}_2 \rightarrow \text{W} + 6\text{HF} \uparrow \]
CVD Reactors
CVD Mechanisms

1 = Diffusion of reactant to surface
2 = Absorption of reactant to surface
3 = Chemical reaction
4 = Desorption of gas by-products
5 = Outdiffusion of by-product gas
Example: Poly-Si Deposition

Figure 14.4  VPE steps include (1) gas-phase decomposition and (2) transport to the surface of the wafer. At the surface the growth species must (3) adsorb, (4) diffuse, and (5) decompose, and (6) the reaction by-products desorb.
CVD Growth Rate Model

Flux across boundary
\[ F_1 = h_G \cdot (C_G - C_S) \]

Flux used in reaction
\[ F_2 = k_S \cdot C_S \]

Normalize to total pressure
\[ Y = \frac{C_{\text{GAS}}}{C_{\text{ALL\_SPECIES}}} = \frac{P_{\text{GAS}}}{P_{\text{GAS\_1}} + P_{\text{GAS\_2}} + \ldots} \]

Thickness growth velocity
\[ v = \frac{F}{N} \]

N = atomic density of film
**Proof:** \( F = \frac{n_1 \overline{v}}{4} - \frac{n_2 \overline{v}}{4} = \frac{\overline{v}}{4} (\lambda \cdot \frac{dn}{dx}) \) where \( \lambda = \) mean free path of gas collision.

\[
F = D \frac{dn}{dx} \Rightarrow D = \frac{\lambda \overline{v}}{2}
\]

Since \( \lambda \propto \frac{kT}{P} \) and \( \overline{v} \propto \sqrt{T} \)

\( \therefore D \propto T^{3/2}/P \)
Mathematical Model for CVD (Cont.)

- Transport parameter $h_G = D/\delta$
  
  $D = \text{gas diffusion constant} = D_0 \cdot T^{3/2} / \text{Pressure}$

- Surface reaction parameter $k_S = k_o \exp (-E_a/kT)$

Balancing $F_1=F_2$

Growth velocity

$$v = \frac{F}{N} = \frac{1}{(1/k_S + 1/h_G)} \frac{C_{\text{ALL\_SPECIES}}}{N}$$

- $C_{\text{ALL\_SPECIES}} = \text{concentration at top of boundary layer}$
- $N = \text{atomic density of deposited material}$

- Limiting cases

  - $k_S << h_G$ Surface Reaction limited
  - $h_G << k_S$ Mass Transport limited
Deposition Rate versus Temp

=log scale Rate

Mass transport limited \( R \propto T^2 \)

Surface-reaction limited \( R \propto e^{-E_A/kT} \)

0

1/ T

high T \( \rightarrow \) low T

Professor N Cheung, U.C. Berkeley
Figure 14.8  Arrhenius behavior of a variety of silicon-containing growth species (after Eversteyn, reprinted by permission, Philips).
Boundary Layer Thickness vs. Distance

\[ \delta_s(x) = \left( \frac{\mu x}{\rho U} \right)^{\frac{1}{2}} \]  

\( \mu = \) viscosity, \( \rho = \) density, \( U = \) velocity

**Figure 9-9** Boundary layer velocities along susceptor. \( \delta_s \) is the thickness of the boundary layer. The boundary layer increases with distance in the direction of the gas flow from Newton's second law. (After [9.2].)

*See handout on CVD Kinetics for derivation*
Average Boundary Layer thickness $<\delta>$

$$<\delta> = \frac{1}{L} \int_0^L \delta(x) \cdot dx = \frac{2}{3} \frac{L}{\sqrt{\rho UL \mu}}$$

$\frac{\rho UL}{\mu} = Re$ is called the Reynold Number of the reactor. When $Re$ is small ($< 2000$), gas flow is viscous. When $Re$ is large ($> 2000$), gas flow is turbulent which is undesirable.

If deposition rate is mass transfer limited,

$$R \propto h_G \propto \frac{1}{<\delta>} \propto \sqrt{U}$$
Growth Rate Dependence on Flow Velocity

mass transport limited

surface reaction limited

\[ V = \frac{F}{N} = \frac{1}{(1/k_S + 1/h_G)} \frac{C_{\text{ALL\_SPECIES}}}{N} Y \]

\[(\text{Gas Flow Rate, } U)^{1/2}\]

Fixed temp T
LPCVD Reactors

Figure 13.18  Basic PECVD geometries: cold wall parallel plate, hot wall parallel plate, and ECR.

(next page)
LPCVD: Low Pressure and high gas velocity due to pumping

Example calculation:
- P reduces ~1000X from 1 atmosphere to ~1 Torr
- Velocity of gas flow U increases ~100X due to pumping

\[ D \propto \frac{1}{P} \quad From\ 760\text{Torr} \rightarrow 1\text{Torr} \quad D \uparrow \text{1000X} \]

\[ \delta \propto \sqrt{\frac{\mu}{\rho U}} = \sqrt{\frac{1000}{100}} \sim 3\text{X} \quad \text{velocity of gas flow 100X} \]

Gas density \( \rho \propto P \quad h_G \rightarrow \frac{1000}{3} \rightarrow 300\text{X} \)

\[ \frac{D}{\delta} \]

Therefore, LPCVD is more likely to be surface reaction limited
(1) $R \uparrow$, since $h_G \uparrow$

(2) More conformal deposition, if $T$ is uniform

(3) Inter-wafer and intra-wafer thickness uniformity less sensitive to gas flow patterns. (i.e. wafer placement).
Gas Flow Issues

(1) $\delta$ depends on gas flow pattern

Furnace tube

wafers

(2) Mass depletion problem

$\text{in} \quad more \quad less \quad \text{out}$
(1) Temperature Ramping along reactor length
For reaction - limited regime:
\[ R(x) = A \exp\left(-\frac{E_A}{kT}\right) \times C(x) \]
[where \( C(x) = \text{SiH}_4 \) Conc.]

\[ \therefore \text{Creating a temperature gradient of 20 - 40°C along the tube will give better uniformity.} \]

(2) Distributed Feed Reactors
PECVD Reactors

[Diagram of PECVD Reactors]

- 2.45 Gz
- ECR magnets
- Temperature-controlled horn and target
- ECR chamber
- Gases in
- Vacuum
- Reaction chamber
- Replaceable chamber liners
- Process position
- Wafer temperature probe
- Wafer load position
- Field-shaping auxiliary magnets
Plasma Enhanced CVD

- Ionized chemical species allows a lower process temperature to be used.
- Film properties (e.g. mechanical stress) can be tailored by controllable ion bombardment with substrate bias voltage.

**DIELECTRIC DEPOSITION PROCESSES**

<table>
<thead>
<tr>
<th>Reaction</th>
<th>LPCVD (°C)</th>
<th>PECVD (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>SiH₄ + NH₃ ⇆ Si₃N₄</td>
<td>850</td>
<td>200-400</td>
</tr>
<tr>
<td>SiH₄ + N₂O ⇆ SiO₂</td>
<td>800</td>
<td>200-400</td>
</tr>
<tr>
<td>TEOS + O₂ ⇆ SiO₂</td>
<td>720</td>
<td>350</td>
</tr>
<tr>
<td>SiH₄ + O₂ ⇆ SiO₂</td>
<td>400</td>
<td></td>
</tr>
</tbody>
</table>
Epitaxial Growth

- Requires an ultra-clean Si surface prior to epi growth.
- Requires deposition of Si at very high temperature for perfect crystallinity.

Processing Temperature
950-1150°C
Strained Si Growth by Heteroepitaxy

Figure 1. Cross-sectional transmission electron microscope images of (a) entire strained Si/substrate structure with (b) close-up of strained silicon device film.
Principle of Atomic Layer Deposition

Self-limiting surface reactions of suitable precursor compounds A and B, which form the desired product S in a binary reaction cycle consisting of two sequential half-reactions.

For an extensive list of precursors, see Ritala and Leskela, Handbook of Thin Film Materials, Vol.1, Chap 2 (2002)
Timing Sequence : CVD vs ALD

<table>
<thead>
<tr>
<th>Conventional CVD Mode</th>
<th>AID Mode</th>
</tr>
</thead>
<tbody>
<tr>
<td>Reactant I</td>
<td>Reactant I</td>
</tr>
<tr>
<td>Reactant II</td>
<td>Reactant II</td>
</tr>
</tbody>
</table>
Spatial ALD

The reactor has separate zones exposing the precursors one by one to a substrate that moves underneath the reactor. Gas bearings between the zones eliminate cross-diffusion and therefore the need for purge steps. Half-reaction timescales are ~10 msec, enabling ultrahigh deposition rates while maintaining ALD film quality.

Source: PV Society, 2010
Possible Spatial ALD Configuration
Example: ZrO₂ ALD

1. The surface is exposed to the first of two gases, here zirconium tetrachloride (ZrCl₄).

2. Molecules of ZrCl₄ adhere to the surface but not to one another.

3. The coated surface is exposed to a second gas, in this case steam (H₂O).

4. The ZrCl₄ on the surface reacts with the water (H₂O) to form a single-molecule-thick veneer of the desired material, zirconium dioxide (ZrO₂).
Step Coverage (Al₂O₃)

Figure 3. ALD features superb step coverage performance. The SEM images show close to 100% conformality for an 18nm thick Al₂O₃ film which was deposited by ALD into high aspect ratio trenches with a minimum lateral dimension of 80nm and a final aspect ratio of ~ 60.
SUMMARY OF THIN FILM MODULE

Vacuum Basics – Mean Free Path and Impingement Rate
Plasma Basics - A plasma sheath above electrode surface which maintains a voltage drop (-10 to -1000V) for ion bombardment

PVD and CVD
Evaporation – Vapor Pressure
Sputtering Deposition- Sputtering Yield, Co-sputtering
PVD Issues – thickness uniformity across wafer, Step Coverage (geometric shadowing, Self Shadowing)
CVD Deposition Rate (h_G versus k_s effects)
CVD Issues – Conformal coverage, Mass depletion

Plasma Enhanced CVD (PECVD) - qualitative
Epitaxial Growth - qualitative
Atomic Layer Deposition (ALD) - qualitative