Chemical Vapor Deposition (CVD)

- Source
- Chemical reaction
- Film
- Substrate

More conformal deposition vs. PVD

(\because \text{higher temp has higher surface diffusion})

Shown here is 100% conformal deposition
(a) \( \text{SiO}_2 \) __gas\[\text{SiH}_4 + \text{O}_2 \rightarrow \text{SiO}_2 + 2\text{H}_2 \uparrow \]

__solid\[\text{gas} \quad 350^\circ\text{C}-500^\circ\text{C}\]

(b) PSG: phospho silicate glass. \([\text{P}_2\text{O}_5 + \text{SiO}_2]\)

\[4\text{PH}_3 + 5\text{O}_2 \rightarrow 2\text{P}_2\text{O}_5 + 6\text{H}_2 \]

\[\text{SiH}_4 + \text{O}_2 \rightarrow \text{SiO}_2 + 2\text{H}_2 \uparrow \]

__350^\circ\text{C}-500^\circ\text{C}\]

(c) TEOS: tetraethylene orthosilicate.

\[\text{Si(OC}_2\text{H}_5)_4 \rightarrow \text{SiO}_2 + C_xH_yO_z \uparrow \]
(d) $Si_3N_4$

$3SiH_4 + NH_3 \rightarrow Si_3N_4 + 12H_2$

(e) Poly - Si

$SiH_4 \xrightarrow{600^\circ C} Si + 2H_2$

(f) W

$WF_6 + 3H_2 \rightarrow W + 6HF \uparrow$
LPCVD Systems
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
**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 Deposition Rate [Grove Model]

\[
\begin{align*}
\frac{D}{\delta} &= h_G \\
k_s &= k_o e^{-\frac{\Delta E}{kT}}
\end{align*}
\]

\[
F_1 = D \left[ C_G - C_S \right] / d \\
F_3 = k_s C_S \\
F_1 = F_3
\]

$d =$ thickness of stagnant layer
\[ F_3 = \frac{k_s h_G}{k_s + h_G} \cdot C_G \]

Film growth rate = \( \frac{F_3}{N} \)

\[ \frac{dx}{dt} = \frac{F_3}{N} = \text{constant with time} \]

(\( cm/sec \))

Note: This result is exactly the same as the Deal-Grove model or thermal oxidation with oxide thickness = 0
Deposition Rate versus Temp

[log scale] Rate

\[ R \propto T^{3/2} \]

- gas transport limited
- surface-reaction limited

high T \rightarrow low T
Boundary Layer Theory for Stagnant Gas Layer

[Planar Geometry]
*See CVD Kinetics Handout for derivation

\[ \delta(x) \] boundary layer thickness
\[ L \] length of the substrate (e.g. substrate or wall of reactor).

For reference only
The gas velocity $u$ is a function of $x$ and $y$ and is equal to zero at plate’s surface and is equal to $U$ in the free gas stream.

Let $\mu = \text{viscosity of gas}$. Then frictional force / unit area along the $x$-direction = $\mu \times \frac{\partial u}{\partial y}$

Let us consider a volume element of unit depth (i.e., into the paper), height $\delta(x)$ and width $dx$.

Total friction force on element = $\mu \times \frac{\partial u}{\partial y} \times (1 \times dx) = \mu \frac{\partial u}{\partial y} \ dx = \text{decelerating force}$

Total accelerating force on element.

$= \rho \times \delta(x)dx \times \frac{du}{dt} = \rho \times \delta(x)dx \times \frac{du}{dx} \times \frac{dx}{dt} = \rho \times \delta(x)dx \times \frac{du}{dx} \times u$

where $\rho$ is the gas mass density

Balanced forces: $\mu \frac{\partial u}{\partial y} = \rho \times \delta(x)u \frac{du}{dx}$ and $u(x,y)$ can be solved exactly.
Approximate Solutions

Let \( \frac{\partial u}{\partial y} \approx \frac{U}{\delta(x)} \); \( \frac{\partial u}{\partial y} \approx \frac{U}{x} \)

Then \( \delta(x) \approx A \left( \frac{\mu x}{\rho Y} \right)^{1/2} - B \)

“parabolic dependence’ where A,B are constants.

The Exact Solution:

The stagnant layer thickness with \( u = 0.99U \) is equal to :

\( \delta(x) \approx 5.0 \left( \frac{\mu x}{U} \right)^{1/2} \)

The “average” boundary layer thickness $\overline{\delta} = \frac{1}{L} \int_0^L \delta(x) \, dx = \frac{2}{3} \frac{L}{\sqrt[3]{\rho U L \mu}} = \frac{2}{3} \sqrt[3]{\frac{L}{\text{Re}_L}}$

$\text{Re}_L$ is called the Reynold Number of the reactor. When $\text{Re}_L$ is small ($\leq 2000$), viscous flow dominates. When $\text{Re}_L$ very large ($\geq 2000$), turbulent flow dominates.
In the CVD growth rate model, it was assumed that mass transport across stagnant layer proceeds by diffusion,

\[ F_1 \equiv D_G \cdot \frac{C_G - C_S}{\delta} \Rightarrow h_G = \frac{D_G}{\delta} \]

where \( D_G \) = diffusivity

For mass-transfer limited deposition, model \( \Rightarrow \)

\[ \frac{dx}{dt} \propto h_G \propto \frac{1}{\delta} \propto \sqrt{U} \]
Figure 14.8  Arrhenius behavior of a variety of silicon-containing growth species (after Eversteyn, reprinted by permission, Philips).
Growth Rate Dependence on Flow Velocity

\[ \text{Growth Rate } \frac{dy}{dt} \]

- mass transport limited
- surface reaction limited

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

![Diagram of LPCVD Reactor]

Figure 13.18 Basic PECVD geometries: cold wall parallel plate, hot wall parallel plate, and ECR.
LPCVD: Low Pressure and high gas velocity due to pumping $h_G \uparrow$

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

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

\[
\delta \propto \sqrt{\frac{\mu}{\rho U}} = \sqrt{\frac{1000}{100}} \sim 3X
\]

\[
\text{velocity of gas flow 100X}
\]

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

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

Therefore, LPCVD is more likely to be **surface reaction limited**
LPCVD Features

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

(2) Mass depletion problem
Solutions

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

∴ Creating a temperature gradient of 20 - 40°C along the tube will give better uniformity.

(2) Distributed Feed Reactors
PECVD Reactors

- 2.45 Gz
- ECR magnets
- Temperature-controlled horn and target
- Gases in
- Vacuum
- Replaceable chamber liners
- Wafer load position
- Wafer temperature probe
- 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**

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<th>LPCVD</th>
<th>PECVD</th>
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<tr>
<td>SiH₄ + NH₃ ⇒ Si₃N₄</td>
<td>850°C</td>
<td>200-400°C</td>
</tr>
<tr>
<td>SiH₄ + N₂O ⇒ SiO₂</td>
<td>800°C</td>
<td>200-400°C</td>
</tr>
<tr>
<td>TEOS + O₂ ⇒ SiO₂</td>
<td>720°C</td>
<td>350°C</td>
</tr>
<tr>
<td>SiH₄ + O₂ ⇒ SiO₂</td>
<td>400°C</td>
<td></td>
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