Chemical Vapor Deposition (CVD)

- Source
- Chemical reaction
- Film
- Substrate

More conformal deposition vs. PVD

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

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

$\text{gas} \quad 350^\circ\text{C}-500^\circ\text{C}$

(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.

$\text{Si} (\text{OC}_2\text{H}_5)_4 \rightarrow \text{SiO}_2 + \text{C}_x\text{H}_y\text{O}_z \uparrow$
(d) \( Si_3N_4 \)

\[ 3 SiH_4 + NH_3 \rightarrow Si_3N_4 + 12 H_2 \]

(e) Poly - Si

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

(f) W

\[ WF_6 + 3 H_2 \rightarrow W + 6 HF \]
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]

\[ D \delta = h_G \]

\[ k_s = k_o e^{-\Delta E/kT} \]

\[ \delta = \text{thickness of stagnant layer} \]

\[ F_1 = D \left[ C_G - C_S \right]/\delta \]

\[ F_3 = k_s C_S \]

\[ F_1 = F_3 \]
\[ F_3 = \frac{1}{\frac{1}{h_G} + \frac{1}{k_s}} \cdot C_G \]

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

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

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

\[ \text{Stream velocity} \]

\[ \text{u} = 0.99 \text{ U} \]

\[ \delta(x) \] 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 = $\mu \times \frac{\partial u}{\partial y} \times (1 \times dx) = \mu \frac{\partial u}{\partial y} dx =$ 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:
\[ \delta(x) \approx 5.0 \left( \frac{\mu x}{U} \right)^{1/2} \]

Average Boundary Layer thickness

\[ \therefore \text{The “average” boundary layer thickness } \overline{\delta} = \frac{1}{L} \int_{0}^{L} \delta(x) \, dx = \frac{2}{3} \sqrt[3]{\frac{\rho U L}{\mu}} = \frac{2}{3} \sqrt{Re_L} \]

\( Re_L \) is called the Reynold Number of the reactor. When \( Re_L \) is small (\( \leq 2000 \)), viscous flow dominates. When \( Re_L \) 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,

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

\[
\text{Growth Rate } \frac{dy}{dt} \text{ vs. } (\text{Gas Flow Rate, } U)^{1/2}
\]

- Mass transport limited
- Surface reaction limited
LPCVD Reactors

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

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

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

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

velocity of gas flow $100X$

Gas density $\rho \propto P$

\[
h_G \rightarrow \frac{1000}{3} \rightarrow 300X
\]

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).
Comments

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

\begin{center}
\begin{tikzpicture}
    \node (tube) at (0,0) {Furnace tube};
    \node (wafers) at (2,-1) {wafers};
    \draw[->] (tube) -- (wafers);
\end{tikzpicture}
\end{center}

(2) Mass depletion problem

\begin{center}
\begin{tikzpicture}
    \node (in) at (-2,-1) {$in$};
    \node (more) at (-1,-1) {more};
    \node (less) at (0,-1) {less};
    \node (out) at (1,-1) {$out$};
    \draw[->] (in) -- (more);
    \draw[->] (more) -- (less);
    \draw[->] (less) -- (out);
\end{tikzpicture}
\end{center}
Solutions for mass depletion problem

(1) Temperature Ramping along reactor length

For reaction-limited regime:

\[ R(x) = A \exp\left[-\frac{\Delta E}{kT}\right] \times C(x) \]  

[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

Process position

Replaceable chamber liners

Wafer load position

Vacuum

Gases in

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

| Reaction          | Deposition Temperature |
|-------------------|--|------------------------|
| SiH$_4$ + NH$_3$  | LPCVD 850°C | PECVD 200-400°C |
| SiH$_4$ + N$_2$O  | LPCVD 800°C | PECVD 200-400°C |
| TEOS + O$_2$      | LPCVD 720°C | PECVD 350°C |
| SiH$_4$ + O$_2$   | LPCVD 400°C | |