Lecture 12: PVD and CVD

(Physical Vapor Deposition and Chemical Vapor Deposition)

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Thin Film Deposition (1)

- Deposition
  - The transformation of vapors into solids, frequently used to grow solid thin film and powder materials

**Physical methods**
- Evaporation
- Sputtering

**Chemical methods**
- Chemical vapor deposition
- Low pressure CVD
- Plasma enhanced CVD

**Applications:**
- Metalization (Al, W, silicide)
- Poly-Si
- Dielectric layers: surface passivation

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Thin Film Deposition (2)

- Physical Vapor Deposition (PVD)
  - Direct impingement of particles on the hot substrate surface
  - Thermal evaporation, electron-beam evaporation, sputtering

- Chemical Vapor Deposition (CVD)
  - Convective heat and mass transfer as well as diffusion with chemical reactions at the substrate surfaces
  - More complex process than PVD
  - More effective in terms of the rate of growth and the quality of deposition
  - LP/AP CVD, Thermal/PE/Ph/LC CVD
PVD : Evaporation (1)

- Thermal evaporator
- Materials: Au, Al, Ti, Cu, Ni, Cr, Ag, Co, Sn, Pd

Deposited film
Evaporated metal
Resistance heater

Thermal Evaporation
Gas Pressure : $10^{-5}$ Torr
PVD : Evaporation (2)

- E-gun evaporator
- Materials: Ti, Cr, Au, Al, Ni, Ag
- Within wafer uniformity: < 5%
- Crucible liner 6pocket crucible

Electron Beam Evaporation
Gas Pressure : $10^{-5}$ Torr
PVD: Sputtering (1)

- Metal sputter
- Materials: Cr, Mo, Ti, Cu, Al, W, Ni, Pt

Gas Pressure: 1~10 mTorr

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PVD : Sputtering (2)

- Wavics sputter
- Materials: Ti, Al, Mo, Cu

- Au sputter
- Materials: Au, Ti (adhesion, Cr (adhesion)
- Within wafer uniformity: < 5%
- Wafer heating: 20°C ~ 250°C
## Thermal evaporation VS Sputtering

<table>
<thead>
<tr>
<th></th>
<th>Thermal Evaporation</th>
<th>Sputtering</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Rate</strong></td>
<td>Thousand atomic layers at a time</td>
<td>On atomic layer at a time</td>
</tr>
<tr>
<td><strong>Choice of materials</strong></td>
<td>Limited</td>
<td>Almost unlimited</td>
</tr>
<tr>
<td><strong>Surface damage</strong></td>
<td>Very low</td>
<td>Ionic bombardment damage</td>
</tr>
<tr>
<td><strong>Adhesion</strong></td>
<td>Poor</td>
<td>Good (on most materials)</td>
</tr>
<tr>
<td><strong>Uniformity</strong></td>
<td>Difficult to control</td>
<td>Easy to control</td>
</tr>
<tr>
<td><strong>Film properties</strong></td>
<td>Difficult to control</td>
<td>Can be controlled by pressure and temperature</td>
</tr>
<tr>
<td><strong>Step coverage</strong></td>
<td><img src="image1" alt="Substrate" /></td>
<td><img src="image2" alt="Substrate" /></td>
</tr>
</tbody>
</table>

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Step coverage problem with PVD (1)

- Geometrical shadowing
Step coverage problem with PVD (2)

- Self-shadowing
Methods for minimizing step coverage problems

1. Rotate +Tilt substrate during deposition

2. Elevate substrate temperature (enhance surface diffusion)

3. Use large-area deposition source
Chemical Vapor Deposition (1)

• What is Chemical Vapor Deposition?
  – Chemical reactions which transform gaseous molecules, called precursor, into a solid material, in the form of thin film or powder, on the surface of a substrate
Chemical Vapor Deposition (2)

More conformal deposition vs. PVD
# CVD Reactor Parameters

<table>
<thead>
<tr>
<th>Parameters</th>
<th>Variations</th>
</tr>
</thead>
<tbody>
<tr>
<td>Temperature range</td>
<td>Low, Medium, High</td>
</tr>
<tr>
<td>Deposition pressure</td>
<td>ATM, Low</td>
</tr>
<tr>
<td>Reactor geometry / Wall temp.</td>
<td>Hot wall, Cold wall</td>
</tr>
<tr>
<td>Energy source</td>
<td>Temp., R.F, UV-light</td>
</tr>
<tr>
<td>Deposition film</td>
<td>Dielectric, Metal</td>
</tr>
<tr>
<td>Reactant / Carrier gases</td>
<td>Metal Organic, Inorganic</td>
</tr>
</tbody>
</table>
Examples: CVD reactors (1)

Vertical CVD Reactor

Horizontal CVD Reactor

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Examples: CVD reactors (2)

Shower head injector

Heater

Dome

Heater

Nozzle injector

Vaporizer

Shower Head

Injector
## CVD systems

<table>
<thead>
<tr>
<th>Type</th>
<th>Advantage</th>
<th>Disadvantage</th>
<th>Usage</th>
<th>Pressure/ temp</th>
</tr>
</thead>
<tbody>
<tr>
<td>APCVD Atmospheric pressure CVD</td>
<td>Simple, fast</td>
<td>Poor step coverage</td>
<td>Low temp oxides</td>
<td>10 ~ 100 kPa 350 ~ 1200 °C</td>
</tr>
<tr>
<td>LPCVD Low pressure CVD</td>
<td>Excellent cleanness, conformity and uniformity</td>
<td>High temp, low deposition rate</td>
<td>Polysilicon, nitride, oxide</td>
<td>100 Pa 550 ~ 600 °C</td>
</tr>
<tr>
<td>PECVD Plasma enhanced CVD</td>
<td>Low temp</td>
<td>Risc for particle and chemical contamination</td>
<td>Low temp oxides, passivation nitrides</td>
<td>200 ~ 600 Pa 300 ~ 400 °C</td>
</tr>
</tbody>
</table>

APCVD is mass transport controlled, LPCVD is surface reaction controlled.

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Atmospheric Pressure CVD

- APCVD (Atmospheric Pressure Chemical Vapor Deposition)
  - High deposition rate, poor uniformity, high contamination level, 250-450 °C
  - Cold wall process
  - Material: epitaxial Si, poly-Si, Si$_3$N$_4$, SiO$_2$, etc.
Low Pressure CVD

• LPCVD (Low Pressure Chemical Vapor Deposition)
  – Low deposition rate, high uniformity, 575-650 °C
  – Good uniformity, property
  – Material: Si$_3$N$_4$, SiO$_2$, poly-Si, etc.
# LPCVD at ISRC (2)

<table>
<thead>
<tr>
<th>Process name</th>
<th>POLY Si</th>
</tr>
</thead>
<tbody>
<tr>
<td>Dep. Temp.</td>
<td>622°C / 624°C / 625°C</td>
</tr>
<tr>
<td>Gas</td>
<td>SiH4 : 60sccm</td>
</tr>
<tr>
<td>Process pressure</td>
<td>270mTorr</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Process name</th>
<th>α - Si</th>
</tr>
</thead>
<tbody>
<tr>
<td>Dep. Temp.</td>
<td>549.5°C / 555°C / 555°C</td>
</tr>
<tr>
<td>Gas</td>
<td>SiH4 : 60 sccm</td>
</tr>
<tr>
<td>Process pressure</td>
<td>250 mTorr</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Process name</th>
<th>Low stress Nitride</th>
</tr>
</thead>
<tbody>
<tr>
<td>Dep. Temp.</td>
<td>825°C / 828°C / 825°C</td>
</tr>
<tr>
<td>Gas</td>
<td>DCS-L: 21sccm, DCS-R: 30sccm,NH3-L:3.5sccm,NH3-L:5sccm</td>
</tr>
<tr>
<td>Process pressure</td>
<td>150mTorr</td>
</tr>
</tbody>
</table>
Plasma Enhanced CVD (1)

• PECVD (Plasma Enhanced Chemical Vapor Deposition)
  – Ionized chemical species allows a lower process temperature.
  – Film properties can be tailored by controllable ion bombardment with substrate bias voltage.
  – Material: Si$_3$N$_4$, SiO$_2$, amorphous-Si, etc.
  – Faster rate and lower deposition temperature than thermal CVD
  – Cracks, pin holes, and poor stoichiometry
Plasma Enhanced CVD at ISRC (2)

- **P-5000 II**

<table>
<thead>
<tr>
<th>RF power (W)</th>
<th>Pressure (Torr)</th>
<th>Gas flow</th>
<th>Dep. Rate (Å/min)</th>
</tr>
</thead>
<tbody>
<tr>
<td>350</td>
<td>9</td>
<td>220</td>
<td>220</td>
</tr>
<tr>
<td></td>
<td></td>
<td>TEOS</td>
<td>O₂</td>
</tr>
</tbody>
</table>

- About 100
Plasma Enhanced CVD at ISRC (3)

**STS PECVD**

<table>
<thead>
<tr>
<th>Nitride</th>
<th>Gas flow (sccm)</th>
<th>Pressure (mTorr)</th>
<th>RF power (W)</th>
<th>Dep. rate (Å/min)</th>
</tr>
</thead>
<tbody>
<tr>
<td>5%SiH$_4$/N$_2$, NH$_3$, N$_2$</td>
<td>800</td>
<td>10</td>
<td>1200</td>
<td>580</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>160</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Oxide</th>
<th>Gas flow (sccm)</th>
<th>Pressure (mTorr)</th>
<th>RF power (W)</th>
<th>Dep. rate (Å/min)</th>
</tr>
</thead>
<tbody>
<tr>
<td>5%SiH$_4$/N$_2$, NH$_3$, N$_2$</td>
<td>160</td>
<td>1500</td>
<td>240</td>
<td>550</td>
</tr>
<tr>
<td></td>
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<td></td>
<td></td>
<td>340</td>
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</tbody>
</table>

<table>
<thead>
<tr>
<th>Oxinitride</th>
<th>Gas flow (sccm)</th>
<th>Pressure (mTorr)</th>
<th>RF power (W)</th>
<th>Dep. rate (Å/min)</th>
</tr>
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<tbody>
<tr>
<td>5%SiH$_4$/N$_2$, NH$_3$, N$_2$</td>
<td>800</td>
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<td>60</td>
<td>580</td>
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<td></td>
<td></td>
<td></td>
<td></td>
<td>300</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Low stress nitride</th>
<th>Gas flow (sccm)</th>
<th>Pressure (mTorr)</th>
<th>RF power (W)</th>
<th>Dep. rate (Å/min)</th>
</tr>
</thead>
<tbody>
<tr>
<td>5%SiH$_4$/N$_2$, NH$_3$, N$_2$</td>
<td>800</td>
<td>10</td>
<td>1200</td>
<td>580</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>100</td>
</tr>
</tbody>
</table>
## Common CVD films

<table>
<thead>
<tr>
<th>Thin film</th>
<th>Typical Reactions</th>
<th>Equipment</th>
<th>Comments</th>
</tr>
</thead>
</table>
| SiO₂      | SiH₄ + O₂ → SiO₂ + H₂  
Si(O₂C₂H₅)₄(+O₃) → SiO₂ + byproducts | LPCVD, PECVD, HDPCVD | 200 ~ 800 °C  
200 ~ 500 °C (LTO) – may require high T anneal.  
25 ~ 400 °C (TEOS-ozone, PECVD, HDPCVD) |
| Si₃N₄     | 3SiH₄ + 4NH₃ → Si₃N₄ + 12H₂  
3SiH₂Cl₂ + 4NH₃ → Si₃N₄ + 6N₂ + 6HCl | LPCVD, PECVD | 650 ~ 800 °C for oxidation mask  
200 ~ 400 °C (PECVD) for passivation |
| Poly-silicon | Same as epitaxial Si | LPCVD | 575 to 800 °C  
Grain structure depends on deposition conditions and doping |
| Epitaxial silicon | SiH₄ → Si + 2H₂  
SiCl₄ + 2H₂ → Si + 4HCl  
Also SiHCl₃, SiH₂Cl₂ | APCVD, LPCVD | 1000 ~ 1250 °C  
If using reduced pressure, 700 to 900 °C |
CVD Chemistries (1)

• Silicon Oxide
  – Dry oxidation: $\text{Si} + \text{O}_2 \rightarrow \text{SiO}_2$
  – Wet Oxidation: $\text{Si} + 2\text{H}_2\text{O} \rightarrow \text{SiO}_2 + 2\text{H}_2$
  – $\text{SiH}_4 + \text{O}_2 \rightarrow \text{SiO}_2 + 2\text{H}_2$
  – $\text{SiH}_4 + \text{N}_2\text{O} \rightarrow \text{SiO}_2 + \text{byproducts}$
  – $\text{SiCl}_2\text{H}_2 + \text{N}_2\text{O} \rightarrow \text{SiO}_2 + \text{byproducts}$
  – $\text{Si(OC}_2\text{H}_5)_4 \rightarrow \text{SiO}_2 + \text{byproducts}$
Example : Silicon dioxide

- Thermally driven reaction
  - Mid-temperature : ~ 500 °C
    - “LTO” (low-temp. oxide) T < ~ 500 °C
  - SiH₄ + O₂ → SiO₂ + H₂
  - Cold-wall, atmospheric, ~ 0.1 μm/min
  - Hot-wall, LPCVD, ~ 0.01 μm/min

- Plasma-enhanced reaction (PECVD)
  - Low temperature : ~ 250 °C

- High temperature: ~ 700 °C
  - Tetraethyl orthosilicate (TEOS)
    - Si(OC₂H₅)₄ → SiO₂ + byproducts
CVD Chemistries (2)

• Silicon Nitride
  – \(3\text{SiH}_4 + 4\text{NH}_3 \rightarrow \text{Si}_3\text{N}_4 + 12\text{H}_2\)
  – \(3\text{SiH}_2\text{Cl}_2 + 4\text{NH}_3 \rightarrow \text{Si}_3\text{N}_4 + \text{byproducts}\)
  – \(3\text{SiH}_4 + 4\text{N}_2\text{O} \rightarrow \text{Si}_3\text{N}_4 + \text{byproducts}\)
  – \(3\text{SiH}_4 + \text{N}_2 \rightarrow \text{Si}_3\text{N}_4 + \text{byproducts}\)
Example: Silicon nitride

**Uses**
- Diffusivity of O$_2$, H$_2$ is very low in nitride
  - Mask against oxidation, protect against water/corrosion
- Diffusivity of Na also very low
  - Protect against mobile ion contamination

**Deposition**
- Stoichiometric formulation is Si$_3$N$_4$
  - In practice Si/N ratio varies from 0.7 (N rich) to 1.1 (Si rich)
- LPCVD: $\sim$ 700 °C $\sim$ 900 °C
  - $3\text{SiH}_4 + 4\text{NH}_3 \rightarrow \text{Si}_3\text{N}_4 + 12\text{H}_2$; $3\text{SiH}_2\text{Cl}_2 + 4\text{NH}_3 \rightarrow \text{Si}_3\text{N}_4 + 6\text{N}_2 + 6\text{HCl}$
  - $\rho$: $\sim$ 3 g/cm$^3$
  - Stress: $\sim$ 10 Gdyne/cm$^2$, tensile
- PECVD
  - $a\text{SiH}_4 + b\text{NH}_3 \rightarrow \text{Si}_x\text{N}_y\text{H}_z + \text{cH}_2$; $a\text{SiH}_4 + b\text{N}_2 \rightarrow \text{Si}_x\text{N}_y\text{H}_z + \text{cH}_2$
  - $\rho$: 2.4 $\sim$ 2.8 g/cm$^3$
  - Stress: $\sim$ 2G $\sim$ 5T Gdyne/cm$^2$
CVD Chemistries (3)

- Poly-silicon: \( \text{SiH}_4 \rightarrow \text{Si} + 2\text{H}_2 \)
- Silicon Carbide
- Polycrystalline Diamond
- Parylene (polymerized p-xylylene)
- Refractory Metals: \( 2\text{WF}_6 + 3\text{SiH}_4 \rightarrow 2\text{W} + 3\text{SiF}_4 + 6\text{H}_2 \)
- II-VI compounds
Example: polysilicon

- **Uses**
  - Gates, high value resistors, “local” interconnects

- **Deposition**
  - Silane pyrolysis: 600 ~ 700 °C, SiH₄ → Si + 2H₂
    - Atmospheric, cold wall, 5% silane in hydrogen, ~1/2 μm/min
    - LPCVD (~ 1 Torr), hot wall, 20 ~ 100% silane, ~ hundreds nm/min
  - Grain size dependent on growth temperature, subsequent processing
    - 950 °C phosphorus diffusion, 20 min; ~ 1 μm grain size
    - 1050 °C oxidation; 1~3 μm grain size

- **In-situ doping**
  - P-type: diborane B₂H₆
    - Can cause substantial increase in deposition rate
  - N-type: arsine AsH₃, phosphine PH₃
    - Can cause substantial decrease in deposition rate

- **Dope after deposition (implant, diffusion)**
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

(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 byproducts are desorbed.

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Kinetics of CVD thin film deposition (1)

- We consider the fluxes for the two important process such as **mass transfer** and **surface reaction**.
- \( F_1 \) = diffusion flux of reactant species to the wafer = mass transfer flux.
  \[
  F_1 = h_G(C_G - C_S)
  \]
  Where \((C_G - C_S)\) term is the difference in concentration of the reactants species between the main gas flow and the wafer surface, and \(h_G\) is the mass transfer coefficient.
- Similarly, \( F_2 \) = flux of reactant consumed by the surface reaction = surface reaction flux.
  \[
  F_2 = K_S C_S
  \]
  Where \(K_S\) is the chemical surface reaction rate and \(C_S\) is the concentration of the reacting species at the surface.
Kinetics of CVD thin film deposition (2)

• In steady state

\[ F_1 = F_2 \Rightarrow C_S = \frac{h_G}{(h_G + k_S)} C_G \]

Growth Rate

\[ R_G = \frac{F_2}{N_{Si}} \quad (N_{Si} : \# \text{ of Si atoms in a unit volume}) \]

\[ R_G = \frac{1}{N_{Si}} \frac{h_G k_S}{h_G + k_S} C_G \]

Surface reaction rate

\[ k_S = k_0 \exp\left(-\frac{E_A}{kT}\right) \]

\( E_A : \text{activation energy} \)

\( k : \text{Boltzmann constant} \)
Kinetics of CVD thin film deposition (3)

• Limiting cases of growth rate

1. If $K_S << h_G$, then we have the surface reaction controlled case:

   $$ R_G = \frac{1}{N_{Si}} k_S C_G $$

2. If $h_G << K_S$, then we have the mass transfer, or gas phase diffusion controlled case:

   $$ R_G = \frac{1}{N_{Si}} h_G C_G $$
Deposition rate versus Temp

- K_S limited deposition is **VERY temp sensitive**.
- h_G limited deposition is **VERY geometry sensitive**.

- Si epi deposition often done at high T to get high quality single crystal growth.
  \[ \therefore \text{h_G controlled.} \]
- Polysilicon is usually deposited at lower temperature surface reaction regime.
Step Coverage Profile (1)

- Step coverage profile

A: Rapid surface migration process (before reaction), yielding uniform coverage since reactants adsorb and move, then react

B: Long mean free path process and no surface migration, with reactant molecule arrival angle determined location on features (local “field of view” effects are important)

C: Short mean free path process with no surface migration, yielding nonconformal coating

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Step Coverage Profile (2)

• Key Parameters
  – Mean Free Path
  – Surface Migration Energy (E ∝ Temperature)
  – Arrival angle

• For conformal step coverage
  – α < l (mean free path)
  – α = arctan (w/z)
  – High Surface Mobility

• Process tendency
  – A: LPCVD
  – B: PECVD

Evaporated & Sputtered Metal
Step Coverage Profile (3)

- Step coverage profile example
Impact of pressure on deposition conditions (1)

- Material arrival angular distribution
  - Depends on mean free path compared to both size of system and size of wafer “steps”
- Case I: “atmospheric pressure”: 760 Torr $\Rightarrow \lambda = 0.07 \, \mu m$
  - Isotropic arrival on ALL surfaces

Assume material does not migrate after arrival.
Impact of pressure on deposition conditions (2)

- Case II: $10^{-1}$ Torr $\Rightarrow \lambda = 0.5$ mm
  - Small compared to system, large compared to wafer features
  - Isotropic arrival at “flat” surface
- But no scattering inside “hole”
  - Shadowing by corners of features
  - “anisotropic” deposition

Assume material does not migrate after arrival.
Impact of pressure on deposition conditions (3)

- Case II: $10^{-5}$ Torr $\Rightarrow \lambda = 5$ m
  - Long compared to almost everything
- Anisotropic arrival at all surfaces
  - Very thin on “side walls”
  - Very dependent on source configuration relative to sample surface

Assume material does not migrate after arrival.
## Dielectric deposition applications summary

<table>
<thead>
<tr>
<th>Application</th>
<th>Film</th>
<th>Requirements</th>
<th>System</th>
</tr>
</thead>
<tbody>
<tr>
<td>Shallow Trench Isolation polish stop layer.</td>
<td>$\text{Si}_3\text{N}_4$</td>
<td>High density film to resist oxidation during trench corner rounding oxidation step.</td>
<td>CVD</td>
</tr>
<tr>
<td>Shallow Trench Isolation trench fill.</td>
<td>$\text{SiO}_2$</td>
<td>High density film with good gap filling properties.</td>
<td>HDP</td>
</tr>
<tr>
<td>Gate polysilicon anti-reflective coating.</td>
<td>$\text{Si}_3\text{N}_4$</td>
<td>Optical properties.</td>
<td>CVD</td>
</tr>
<tr>
<td>Sidewall spacers.</td>
<td>$\text{Si}_3\text{N}_4$</td>
<td>Etch rate difference relative to $\text{SiO}_2$.</td>
<td>CVD</td>
</tr>
<tr>
<td>Intermetal Dielectric layer 0 etch stop.</td>
<td>$\text{Si}_3\text{N}_4$</td>
<td>High density film with good barrier properties and etch rate difference relative to $\text{SiO}_2$.</td>
<td>HDP</td>
</tr>
<tr>
<td>Intermetal Dielectric layer 0.</td>
<td>Doped $\text{SiO}_2$</td>
<td>Thick film without cracking. Typically phosphorus doped or borophosphorous doped $\text{SiO}_2$.</td>
<td>PECVD</td>
</tr>
<tr>
<td>Intermetal Dielectric layer 1+ with aluminum lines.</td>
<td>$\text{SiO}_2$</td>
<td>Good gap fill.</td>
<td>HDP</td>
</tr>
<tr>
<td>Intermetal Dielectric film 1+ with damascene copper.</td>
<td>$\text{FSG}$ or $\text{SiOC}$</td>
<td>Low-k films such as fluorine doped oxide or carbon doped oxide. Can be deposited with HDP or PECVD. PECVD is preferred due to lower complexity although many FSG films were deposited in HDP system already installed in fabs from previous generation products.</td>
<td>HDP or PECVD.</td>
</tr>
<tr>
<td>Intermetal Dielectric film 1+ etch stop layer.</td>
<td>$\text{Si}_3\text{N}_4$ or $\text{SiC}$</td>
<td>Etch rate difference relative to FSG or SiOC. Lowest k value possible also desired.</td>
<td>PECVD</td>
</tr>
<tr>
<td>Passivation</td>
<td>$\text{Si}_3\text{N}_4$</td>
<td>Good barrier properties</td>
<td>PECVD</td>
</tr>
</tbody>
</table>
## Common CVD deposition reactants

<table>
<thead>
<tr>
<th>Film</th>
<th>Reactants</th>
<th>System</th>
<th>Composition</th>
<th>Step coverage</th>
<th>Temperature (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Al</td>
<td>TIBA, DIBAH, DMAH</td>
<td>LPCVD</td>
<td>--</td>
<td>Conformal</td>
<td>&lt;250</td>
</tr>
<tr>
<td>Cu</td>
<td>Cu(hfac)$_2$ + H$_2$ or Cu$^1$(hfac)L</td>
<td>LPCVD</td>
<td>--</td>
<td>Conformal</td>
<td>350-450</td>
</tr>
<tr>
<td>Si</td>
<td>SiH$_4$</td>
<td>APCVD</td>
<td>Crystalline</td>
<td>--</td>
<td>950-1,050</td>
</tr>
<tr>
<td></td>
<td>SiCl$_2$H$_2$</td>
<td>APCVD</td>
<td>Crystalline</td>
<td>--</td>
<td>1,050-1,150</td>
</tr>
<tr>
<td></td>
<td>SiHCl$_3$</td>
<td>APCVD</td>
<td>Crystalline</td>
<td>--</td>
<td>1,100-1,200</td>
</tr>
<tr>
<td></td>
<td>SiCl$_4$</td>
<td>APCVD</td>
<td>Crystalline</td>
<td>--</td>
<td>1,150-1,250</td>
</tr>
<tr>
<td></td>
<td>SiH$_4$</td>
<td>LPCVD</td>
<td>Crystalline</td>
<td>--</td>
<td>550-700</td>
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<tr>
<td></td>
<td>SiH$_4$</td>
<td>LPCVD</td>
<td>Polycrystalline</td>
<td>Conformal</td>
<td>580-650</td>
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<tr>
<td>Si$_3$N$_4$</td>
<td>--</td>
<td>--</td>
<td>--</td>
<td>--</td>
<td>50-250</td>
</tr>
<tr>
<td></td>
<td>SiH$_4$ + NH$_3$</td>
<td>PECVD</td>
<td>Si$_x$N$_y$H$_z$</td>
<td>Non Conformal?</td>
<td>50-200</td>
</tr>
<tr>
<td></td>
<td>SiH$_4$ + NH$_3$ + N$_2$O</td>
<td>PECVD</td>
<td>Si$_x$O$_y$N$_z$</td>
<td>Non Conformal?</td>
<td>250-350</td>
</tr>
<tr>
<td></td>
<td>SiCl$_2$H$_2$ + NH$_3$</td>
<td>LPCVD</td>
<td>Si$_3$N$_4$(H)</td>
<td>Conformal</td>
<td>700-800</td>
</tr>
<tr>
<td>SiO$_2$</td>
<td>SiH$_4$+N$_2$O</td>
<td>PHCVD</td>
<td>SiO$_2$</td>
<td>--</td>
<td>50-200</td>
</tr>
<tr>
<td></td>
<td>SiH$_4$ + O$_2$ or SiH$_4$ + N$_2$O</td>
<td>PECVD</td>
<td>SiO$_1$9(H)</td>
<td>Non Conformal</td>
<td>250-400</td>
</tr>
<tr>
<td></td>
<td>TEOS + O$_2$</td>
<td>PECVD</td>
<td>SiO$_x$</td>
<td>Conformal</td>
<td>400</td>
</tr>
<tr>
<td></td>
<td>TEOS + O$_2$</td>
<td>APCVD</td>
<td>SiO$_2$(-OH)</td>
<td>Isotropic flow</td>
<td>400</td>
</tr>
<tr>
<td></td>
<td>SiH$_4$ + O$_2$</td>
<td>APCVD</td>
<td>SiO$_2$(H)</td>
<td>Non conformal</td>
<td>450</td>
</tr>
<tr>
<td></td>
<td>TEOS + O$_2$</td>
<td>LPCVD</td>
<td>SiO$_2$(-OH)</td>
<td>Conformal</td>
<td>700</td>
</tr>
<tr>
<td></td>
<td>SiCl$_2$H$_2$ + N$_2$O</td>
<td>LPCVD</td>
<td>SiO$_2$(Cl)</td>
<td>Conformal</td>
<td>900</td>
</tr>
<tr>
<td></td>
<td>O$_2$ or H$_2$O</td>
<td>Thermal</td>
<td>SiO$_2$</td>
<td>Conformal</td>
<td>700-1,200</td>
</tr>
<tr>
<td>TiN</td>
<td>TiCl$_2$ + NH$_3$ or TiCl$_3$ + H$_2$/N$_2$ or TDMAT + NH$_3$</td>
<td>LPCVD</td>
<td>--</td>
<td>Conformal</td>
<td>400-700, or &gt;700</td>
</tr>
<tr>
<td>W</td>
<td>WF$_6$ + SiH$_4$ or WF$_6$ + H$_2$</td>
<td>LPCVD</td>
<td>--</td>
<td>Conformal</td>
<td>400-500</td>
</tr>
</tbody>
</table>
**CVD Hazards**

- Many gases used in CVD systems are toxic (hazardous to humans), corrosive (causes corrosion to stainless steel and other metals), flammable (burns when exposed to an ignition source and an oxygen source), explosive and/or pyrophoric (spontaneously burn or explode in air, moisture or when exposed to oxygen).

<table>
<thead>
<tr>
<th>Gas</th>
<th>Formula</th>
<th>Hazard</th>
<th>Flammable limits in air (%vol)</th>
<th>Exposure limit (ppm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ammonia</td>
<td>NH₃</td>
<td>toxic, corrosive</td>
<td>16–25</td>
<td>25</td>
</tr>
<tr>
<td>Argon</td>
<td>Ar</td>
<td>inert</td>
<td>—</td>
<td>—</td>
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<tr>
<td>Arsine</td>
<td>AsH₃</td>
<td>toxic</td>
<td>—</td>
<td>0.05</td>
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<tr>
<td>Diborane</td>
<td>B₂H₆</td>
<td>toxic, flammable</td>
<td>1–98</td>
<td>0.1</td>
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<tr>
<td>Dichlorosilane</td>
<td>SiH₂Cl₂</td>
<td>flammable, toxic</td>
<td>4–99</td>
<td>5</td>
</tr>
<tr>
<td>Hydrogen</td>
<td>H₂</td>
<td>flammable</td>
<td>4–74</td>
<td>—</td>
</tr>
<tr>
<td>Hydrogen chloride</td>
<td>HCl</td>
<td>corrosive, toxic</td>
<td>—</td>
<td>5</td>
</tr>
<tr>
<td>Nitrogen</td>
<td>N₂</td>
<td>inert</td>
<td>—</td>
<td>—</td>
</tr>
<tr>
<td>Nitrogen oxide</td>
<td>N₂O</td>
<td>oxidizer</td>
<td>—</td>
<td>—</td>
</tr>
<tr>
<td>Oxygen</td>
<td>O₂</td>
<td>oxidizer</td>
<td>—</td>
<td>—</td>
</tr>
<tr>
<td>Phoshpine</td>
<td>PH₃</td>
<td>toxic, flammable</td>
<td>—</td>
<td>pyrophoric 0.3</td>
</tr>
<tr>
<td>Silane</td>
<td>SiH₄</td>
<td>flammable, toxic</td>
<td>—</td>
<td>pyrophoric 0.5</td>
</tr>
</tbody>
</table>
Reference

- http://www.dowcorning.co.jp
Reference

Reference

- http://chiuserv.ac.nctu.edu.tw/~htchiu/cvd/home.html
- http://www.plasmas.org