Text Book:
Silicon VLSI Technology
Fundamentals, Practice and Modeling
Authors: J. D. Plummer, M. D. Deal, and P. B. Griffin
Thin Film Deposition – Introduction

- Many films, made of many different materials are deposited during a standard CMOS process.
  - Epi layer, Si, SiO₂, contact materials, metals
- Requirements or desirable traits for deposition:
  1. Desired composition, low contaminates, good electrical and mechanical properties.
  2. Uniform thickness across wafer, and wafer-to-wafer.
  3. Good step coverage ("conformal coverage").
  5. Planarized films.
### Roadmap

![Diagram of metal line and contact hole with aspect ratio formula](aspect_ratio.png)

\[ \text{Aspect ratio} = AR = \frac{h}{w} \]

<table>
<thead>
<tr>
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<th></th>
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</thead>
<tbody>
<tr>
<td>Technology Node (half pitch)</td>
<td>250 nm</td>
<td>180 nm</td>
<td>130 nm</td>
<td>90 nm</td>
<td>65 nm</td>
<td>45 nm</td>
<td>32 nm</td>
<td>22 nm</td>
<td>18 nm</td>
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<tr>
<td>MPU Printed Gate Length</td>
<td>100 nm</td>
<td>70 nm</td>
<td>53 nm</td>
<td>35 nm</td>
<td>25 nm</td>
<td>18 nm</td>
<td>13 nm</td>
<td>10 nm</td>
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<tr>
<td>Min Metal 1 Pitch (nm)</td>
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<td>152</td>
<td>108</td>
<td>76</td>
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<tr>
<td>Wiring Levels - Logic</td>
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<td>11</td>
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<td>14</td>
<td>14</td>
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<tr>
<td>Metal 1 Aspect Ratio (Cu)</td>
<td>1.7</td>
<td>1.7</td>
<td>1.8</td>
<td>1.9</td>
<td>2.0</td>
<td>2.0</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Contact Aspect Ratio (DRAM)</td>
<td>15</td>
<td>16</td>
<td>&gt;20</td>
<td>&gt;20</td>
<td>&gt;20</td>
<td>&gt;20</td>
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<tr>
<td>STI Trench Aspect Ratio</td>
<td>4.8</td>
<td>5.9</td>
<td>7.9</td>
<td>10.3</td>
<td>14</td>
<td>16.4</td>
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<tr>
<td>Metal Resistivity (µohm-cm)</td>
<td>3.3, 2.2</td>
<td>2.2</td>
<td>2.2</td>
<td>2.2</td>
<td>2.2</td>
<td>2.2</td>
<td>2.2</td>
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<td>2.2</td>
</tr>
<tr>
<td>Interlevel Dielectric Constant</td>
<td>3.9</td>
<td>3.7</td>
<td>3.7</td>
<td>&lt;2.7</td>
<td>&lt;2.4</td>
<td>&lt;2.1</td>
<td>&lt;1.9</td>
<td>&lt;1.7</td>
<td>&lt;1.7</td>
</tr>
</tbody>
</table>

- Note the aspect ratios and the need for new materials.
- Note also the number of metal layers requiring more deposition steps.

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Thin Film Deposition

- Quality – composition, defect density, mechanical and electrical properties
- Uniformity – affect performance (mechanical, electrical)

- Voids: Trap chemicals lead to cracks (dielectric) large contact resistance and sheet resistance (metallization)
- AR (aspect ratio) = $h/w \uparrow$ with \downarrow feature size in ICs.

$$Aspect\, ratio = AR = \frac{h}{w}$$
Examples Thin Film Depositions

Thinning causes metal resistance to increase, generates heat and lead to failure.

Figure 9-3 SEM images of coverage and filling problems. (a) shows poor step coverage of a TiW/Al/TiW metal stack layer, deposited by sputter deposition, over an oxide step. (b) shows voids in a Chemical Vapor Deposition (CVD) oxide layer for narrow spaces between metal lines. Photos courtesy of VLSI Technology, Inc.
Basic Concepts

Two main deposition methods are used today:
1. Chemical Vapor Deposition (CVD)
   - APCVD, LPCVD, PECVD, HDPCVD
2. Physical Vapor Deposition (PVD)
   - evaporation, sputter deposition

Chemical Vapor Deposition (CVD)

AP-CVD - Atmospheric Pressure CVD
- Cold wall reactor
- Heated susceptor

LPCVD - Low Pressure CVD

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Atmospheric Pressure Chemical Vapor Deposition

1. Transport of reactants to the deposition region.
2. Transport of reactants from the main gas stream through the boundary layer to the wafer surface.
3. Adsorption of reactants on the wafer surface.
4. Surface reactions, including: chemical decomposition or reaction, surface migration to attachment sites (kinks and ledges); site incorporation; and other surface reactions (emission and redeposition for example).
5. Desorption of byproducts.
6. Transport of byproducts through boundary layer.
7. Transport of byproducts away from the deposition region.
Wafer Surface Region

\[ F_1 = \text{diffusion flux of reactant species to the wafer} = \text{mass transfer flux, step 2} \]
\[ F_1 = h_G (C_G - C_S) \]  \hspace{1cm} (4)
where \( h_G \) is the mass transfer coefficient (in cm/sec).

\[ F_2 = \text{flux of reactant consumed by the surface reaction} = \text{surface reaction flux, steps 3-5} \]
\[ F_2 = k_s C_S \]  \hspace{1cm} (5)
where \( k_s \) is the surface reaction rate (in cm/sec).

In steady state:
\[ F = F_1 = F_2 \]  \hspace{1cm} (6)

Equating Equations (4) and (5) leads to
\[ C_S = C_G \left( \frac{1 + \frac{k_s}{h_G}}{} \right)^{-1} \]  \hspace{1cm} (7)

The growth rate of the film is now given by
\[ v = \frac{F}{N} = \frac{k_s h_G C_G}{k_s + h_G} \left( \frac{C_T}{N} \right) = \frac{k_s h_G C_T}{k_s + h_G} \left( \frac{Y}{N} \right) \]  \hspace{1cm} (8)

where \( N \) is the number of atoms per unit volume in the film (5 \( \times \) 10^{22} cm\(^{-3}\) for the case of epitaxial Si deposition) and \( Y \) is the mole fraction (partial pressure/total pressure) of the incorporating species.

\[ Y = \frac{C_A}{C_T} \] Mole fraction of the incorporating species in the gas phase.

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Growth Kinetics - Temperature

\[ v = \frac{F}{N} = \frac{k_s h_g}{k_s + h_g} \frac{C_i}{N} = \frac{k_s h_g}{k_s + h_g} \frac{C_i}{N} Y \]

1. If \( k_s \ll h_g \), then we have the surface reaction controlled case (fast transport, slow reaction):

\[ v \equiv \frac{C_i}{N} k_s Y \]  \hspace{1cm} (9)

2. If \( h_g \ll k_s \), then we have the mass transfer or gas phase diffusion, controlled case (slow transport, fast reaction):

\[ v \equiv \frac{C_i}{N} h_g Y \]  \hspace{1cm} (10)

- The surface term is Arrhenius with \( E_A \) depending on the particular reaction (1.6 eV for single crystal silicon deposition).

- \( h_g \) is \( \approx \) constant (diffusion through boundary layer).

- As an example, Si epitaxial deposition is shown below (at 1 atm. total pressure). Note same \( E_A \) values and \( h_g \approx \) constant. Rate is roughly proportional to (mol. wt.)\(^{1/2}\).
Experimental Si Deposition

Key points:

- $k_g$ limited deposition is VERY temp sensitive.
- $h_0$ limited deposition is VERY geometry (boundary layer) sensitive.

- Si epi deposition often done at high T to get high quality single crystal growth.
  - $h_0$ controlled.
  - horizontal reactor configuration.

- There is a substrate orientation effect when growing Si. Fewer surface bonds (e.g. <111>) means slower growth rate.

- $h_0$ corresponds to diffusion through a boundary layer of thickness $\delta_S$. 

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Boundary Layer – Diffusion to the Surface

Gas moves with the constant velocity $U$.

Boundary layer (caused by friction) increases along the susceptor, mass transfer coefficient $h_t$ decreases, gas depletion caused by consumption of the reacting species (concentrations decrease).

Therefore, growth rate decreases along the chamber:
- Use tilted susceptor
- Use T gradient 5-25°C
- Gas injectors along the tube
- Use moving belt

Deposition of alloys DIFFICULT – various reactions, kinetics (species, precursors)
- Use Physical-VD rather than CVD
Doping in CVD for EPITAXY (Intentional and Unintentional)

The dopant sources at the surface go through:
- dissociation of hydride gas
- lattice site incorporation
- burying of dopants by other atoms in the film

Simulation very inaccurate: chamber design etc.

In deposition, the doping,
- \( C \propto P_f \) for low growth rates
- \( C \propto \frac{P_f}{v} \) for high growth rates

T & time of CVD

Calculate all distributions (contributions) to get \( C(x,t) \)

\[
C(x,t) = \frac{C_0}{\sqrt{2\pi D_f t}} \exp\left(-\frac{x^2}{2D_ft}\right)
\]

\( \nu \gg \sqrt{D_f} \)

The growth is faster than the diffusion
Low Pressure Chemical Vapor Deposition (LPCVD)

- Atmospheric pressure systems have major drawbacks:
  - At high T, a horizontal configuration must be used (few wafers at a time).
  - At low T, the deposition rate goes down and throughput is again low.

- The solution is to operate at low pressure. In the mass transfer limited regime,
  \[ h_G = \frac{D_G}{\delta_S} \quad \text{But} \quad D_G \propto \frac{1}{P_{total}} \] (12)

- \( D_G \) will go up 760 times at 1 torr, while \( \delta_S \) increases by about 7 times. Thus \( h_G \) will increase by about 100 times.
- Transport of reactants from gas phase to surface through boundary layer is no longer rate limiting.
- Process is more T sensitive, but can use resistance heated, hot-walled system for good control of temperature and can stack wafers.
Plasma-Enhanced CVD

- Plasmas has been used for cutting and etching, but the concept can be applied to any operation.
- For CVD, a plasma can be used to increase the deposition rate in an environment where the temperature of the substrate must not be significantly elevated.
  - Once metals have been applied, the wafer should not be raised above the melting point of the metal. Typical temperatures for dielectric deposition are from 200 to 350 deg. C.
  - Depositing material without significantly effecting the Dt
- Plasma consists of electrons, ionized molecules, neutral molecules, neutral and ionized fragments of broken-up molecules, excited molecules and free radicals.
- In a plasma, additional energy from the plasma constituents is added to the reactant gases, increasing their energy and the effective deposition rate.
- Free radicals are electrically neutral species that have incomplete bonding and are extremely reactive. (e.g. SiO, SiH3, F)
Plasma Enhanced CVD (PECVD)

- Non-thermal energy to enhance processes at lower temperatures.
  - May be required. Al melting point is 660 deg. C.
- The net result from the fragmentation, the free radicals, and the ion bombardment is that the surface processes and deposition occur at much lower temperatures than in non-plasma systems.
High Density Plasma (HDP) CVD

- Newly developed version of PECVD.
- Remote high density plasma with independent RF substrate bias.
- Allows simultaneous deposition and sputtering for better planarization and void-free films (later).
- Mostly used for SiO₂ deposition in backend processes.
Physical Vapor Deposition (PVD)

- PVD uses mainly physical processes to produce reactant species in the gas phase and to deposit films.
- In evaporation, source material is heated in high vacuum chamber. (P < 10^-5 torr).
- Mostly line-of-sight deposition since pressure is low.
- Deposition rate is determined by emitted flux and by geometry of the target and wafer holder.
- Advantages:
  - Little damage
  - Pure layers (high vacuum)
- Disadvantages:
  - Not for low vapor pressure metals
  - No in-situ cleaning
  - Poor step coverage

- Purer – no filaments, only surface of the source melted
- X-rays generated \( \Rightarrow \) trapped charges in the gate oxides \( \Rightarrow \) must be annealed
Evaporation

- The evaporation source can be considered either a point source or as a small area surface source (latter is more applicable to most evaporation systems).

\[ F_k^p = \frac{R_{\text{evap}}}{\Omega \cdot r^2} \]

\[ V = \frac{R_{\text{evap}}}{\Omega \cdot N \cdot r^2} \cdot \cos \theta \]

- \( \Omega \) is the solid angle over which the source emits (4\( \pi \) if all directions, 2\( \pi \) if only upwards); \( N \) is the density of the material being deposited.

- The outward flux \( F_k^p \) from a point source, is independent of angle, \( \theta_i \), while the outward flux from a small area surface source, varies as \( \cos(\theta_i) \) or even \( \cos(\theta_i)^n \).
Evaporation (2)

- Nonuniform deposition using a linear target
- Relative normalized deposition rate for a point source and a surface source.

Figure 9-17: Deposition rate of evaporated film as a function of position on substrate for point and surface sources. $R = R_0$ in this configuration for both point and surface sources.
Evaporation (3)

- Deviations from ideal point-sources or small-area surface source emissions can occur.
- For a small area surface source, the ideal emission varies as $\cos(\theta)$, referred to as Knudsen-cell-like behavior.
- Further deviation or non-ideal behavior may vary as $\cos(\theta)^n$.

![Diagram]

a. Uniform (isotropic) emission from a point source
b. Ideal cosine emission from a small planar surface source. ($n = 1$ in $\cos^0\theta$ distribution)
c. Non-ideal, more anisotropic emission from a small planar surface source. ($n > 1$ in $\cos^n\theta$ distribution)
Vapor Pressure – Evaporation Rate

- With evaporation:
  - Can evaporate just about any element but.
  - Difficult to evaporate alloys and compounds
  - Step coverage is poor (line of sight and sticking coefficient of $Sc=1$).
- E-beam and sputtering used instead of PVD

\[
R_{\text{evap}} = 5.83 \times 10^{-2} \cdot A_{\text{source}} \left( \frac{m}{T} \right)^{3/2} \cdot P_a
\]

Evaporation rate of common materials in torr

\[
S_c = \frac{I_{\text{actual}}}{I_{\text{incident}}}
\]

$S_c = 1$  \hspace{1cm} $S_c < 1$
DC Sputter Deposition

- Uses plasma to sputter target, dislodging atoms which then deposit on wafers to form film.
- A major IC technique for alloys (Al, W, Ti, silicides, etc.)
- Higher pressures than evaporation (1-100 mtorr vs. < 10^{-5} torr).
- The plasma contains ≈ equal numbers of positive argon ions and electrons as well as neutral argon atoms.
DC Sputter Deposition (2)

- Similar to PECVD

- Ar⁺ ions are accelerated across cathode sheath to the negatively charged cathode, striking that electrode (the “target”) and sputtering off atoms (e.g. Al).

- Most of voltage drop of the system (due to applied DC voltage, $V_e$) occurs over cathode sheath.

- The atoms travel through plasma and deposit on wafers sitting on anode.
DC Sputter Deposition (3)

- Ar⁺ ions are accelerated across cathode sheath to the negatively charged cathode, striking that electrode (the “target”) and sputtering off atoms (e.g. Al).
- The atoms travel through plasma and deposit on wafers sitting on anode.
- Rate of sputtering depends on the sputtering yield, Y, defined as the number of atoms or molecules ejected from the target per incident ion.
- Y is a function of the energy and mass of ions, and the target material. It is also a function of incident angle.
DC Sputtering Targets & Wafers

- Sputtering targets are generally large and provide a wide range of arrival angles in contrast to a point source.
  a) Isotropic flux arrival
  \[ n = 1 \cos^0 \] arrival angle distribution
  b) Anisotropic flux arrival
  \[ n > 1 \cos^0 \] arrival angle distribution

- Arrival angle distribution generally described by \[ \cos^n \theta \] distribution (the normal component of flux striking the surface determines the deposition or growth rate).
- Size and type of source, system geometry and collisions in gas phase important in arrival angle distribution.
RF Sputter Deposition

- For DC sputtering, target electrode is conducting.
- To sputter dielectric materials use RF power source.

- Due to slower mobility of ions vs. electrons, the plasma biases positively with respect to both electrodes. (DC current = zero.)
- Continuous sputtering.
- When the electrode areas are not equal, the field must be higher at the smaller electrode (higher current density), to maintain overall current continuity
  \[ \frac{V_1}{V_2} = \left( \frac{A_2}{A_1} \right)^m \]  
  (m = 1-2 experimentally) (13)

- Thus by making the target electrode smaller, sputtering occurs "only" on the target. Wafer electrode can also be connected to chamber walls, further increasing \( V_2/V_1 \).
Ionized Sputter Deposition or HDP Sputtering

- In some systems the depositing atoms themselves are ionized. An RF coil around the plasma induces collisions in the plasma creating the ions.

- This provides a narrow distribution of arrival angles which may be useful when filling or coating the bottom of deep contact hole.
### Table 9-1: Common deposition methods for thin films in integrated circuit fabrication

<table>
<thead>
<tr>
<th>Thin Film</th>
<th>Equipment</th>
<th>Typical Reaction</th>
<th>Comments</th>
</tr>
</thead>
<tbody>
<tr>
<td>Epitaxial silicon</td>
<td>LPCVD, LPICVD</td>
<td>SiH₄ + H₂ → Si + 2H₂</td>
<td>700-1250°C</td>
</tr>
<tr>
<td>Polysilicon</td>
<td>LPCVD</td>
<td>SiCl₄ + H₂ → Si + 2HCl</td>
<td>Reduce pressure for lower-temperature deposition, 157-350°C</td>
</tr>
<tr>
<td>AlN</td>
<td>LPCVD, PECD</td>
<td>3SiH₄ + NH₃ → SiNₓ + 12H₂</td>
<td>485-650°C for oxidation mask, 200-400°C (PECVD) for passivation, 200-500°C</td>
</tr>
<tr>
<td>Si₃N₄</td>
<td>LPCVD, PECD, HDPCVD, LPCVD</td>
<td>SiH₄ + O₂ → SiO₂ + 2H₂</td>
<td>200-300°C (LTE) may require high T extension, 25-450°C (TEOS-oxide, PECVD, HDPCVD)</td>
</tr>
<tr>
<td>Al</td>
<td>Magnetron sputter deposition</td>
<td></td>
<td>35-300°C (standard deposition), 440-550°C (hot Al) to sinter-alloy</td>
</tr>
<tr>
<td>Ti and Ti-W</td>
<td>Magnetron sputter deposition (standard, ionized, or collimated)</td>
<td></td>
<td>CVB difficult, nitrogen can be added to Ti-W to assist grain formation</td>
</tr>
<tr>
<td>W</td>
<td>LPCVD</td>
<td>2WF₆ + 3NH₃ → W + 6HF</td>
<td>200-500°C</td>
</tr>
<tr>
<td>Si₃N₄</td>
<td>LPCVD</td>
<td>Wₕ + 3H₂ → W + 6HF</td>
<td>200-500°C</td>
</tr>
<tr>
<td>TiSi₂</td>
<td>Sputter and surface reaction</td>
<td>Ti (substrate) + Si (sputtered) → TiSi₂</td>
<td>Solid ultra-thin</td>
</tr>
<tr>
<td>TIN</td>
<td>Coating or CVB</td>
<td>Tlₙ + Nₙ (in plasma) → TIN</td>
<td>Organometallic source possible for MOVCD deposition, 200°C also formed in TIN process</td>
</tr>
<tr>
<td>Cu</td>
<td>Electroplating, electrophoretic deposition, CVB</td>
<td>Cu⁺⁺ + 2e⁻ → Cu</td>
<td>Electroplating is most common method today</td>
</tr>
</tbody>
</table>
Manufacturing Methods

- Epitaxial Silicon Deposition
  - Requires access to crystalline surface, or else amorphous Si (a-Si) or polycrystalline Si will result
  - CVD of silane or silicon tetrachloride
    - APCVD or LPVD
- Polycrystalline Silicon Deposition
  - Deposited on arbitrary surfaces
  - Sputtered or CVD with less restrictive conditions that epi
  - TEM of grain structure and resistivity follow
Polycrystalline Silicon

a) Undoped thin grains in columns
b) Phosphorous doped with larger grains
c) Undoped and annealed showing little grain grown with annealing
d) Phosphorous doped and annealed showing grain growth with annealing

Figure 9-32 TEM cross sections of CVD polycrystalline films deposited at 625°C: (a) as-deposited, undoped film, showing thin grains in a columnar structure; (b) as-deposited phosphorus-doped film, showing much larger grain size; (c) annealed (1000°C), undoped film, showing little grain growth as compared to (a); (d) annealed (1000°C), phosphorus-doped film, showing evidence of grain growth as compared to (b). Reprinted with permission of the Electrochemical Society [3,19].

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Polycrystalline Silicon Conductivity

- Due to the low resistivity when doped, "poly" has been used both as a gate for MOS transistors and a conductor.

*Figure 9-33* Resistivity of annealed phosphorus-implanted silicon films as a function of phosphorus concentration. LP refers to LPCVD deposition, AP refers to APCVD deposition, and the numbers in the labels refer to the deposition temperature. (After [9.21].)
Manufacturing Methods (2)

- **Silicon Nitride Deposition**
  - Films used as a mask against oxidation or as a final passivation layer. A good barrier to water and sodium diffusion.
  - Generally not used in direct contact with silicon due to poor interface properties.
  - LPCVD or PECVD

- **Silicon Dioxide Deposition**
  - Low temperature CVD for dielectric isolation, separating conductive layers. Therefore LPCVD and PECVD typical.
  - HDP CVD also being used
Manufacturing Methods (3)

- **Al Deposition**
  - A main interconnect material (being replaced by copper)
  - DC magnetron sputtering
- **Titanium (Ti) and Titanium-Tungsten (Ti-W)**
  - An underlay for contacts and vias between interconnect layers.
  - Typically deposited by sputtering
- **Tungsten**
  - Contact or via conductor, tungsten via plugs are common
  - CVD using hot-wall and low pressure
- **TiSi$_2$ and WSi$_2$ Deposition**
  - Silicides of titanium and tungsten. Used to reduce resistivity of polysilicon lines and lower contact resistances with doped N and P regions.
  - Sputtering, co-sputtering, co-evaporation or CVD
Manufacturing Methods (4)

- TiN Deposition
  - Barrier layer in contacts and as an under layer and antireflective layer in interconnects. A very hard metal that can be highly stressed but is brittle.
  - Sputtered using reactive sputtering techniques or CVD
- Copper Deposition
  - The most recent interconnect metal – lower resistivity and less electromigration than Aluminum.
  - PVD by both sputtering and evaporation. CVD possible. Electrolytic plating or electroless deposition
Models and Simulation

- Within the past decade, a number of simulation tools have been developed for topography simulation.

- Generalized picture of fluxes involved in deposition. (No gas phase boundary layer is included, so this picture doesn't fully model APCVD.)

- Essentially the same picture will be used for etching simulation (in Chapter 10).

\[
F_{\text{net}} = F_{\text{direct\( (\text{neutral}) \)}} + F_{\text{direct\( (\text{ion}) \)}} + F_{\text{redepos}} + F_{\text{diff\, in}}
- F_{\text{emitted}} - F_{\text{spattered}} - F_{\text{diff\, out}}
\]  

(14)

- To simulate these processes, we need mathematical descriptions of the various fluxes.
- Modeling specific systems involves figuring out which of these fluxes needs to be included.
- Stanford Profile Emulator for Etching and Deposition in IC Engineering (SPEEDIE) used in text for material
Considering Incoming Fluxes: Direct

- Direct fluxes are generally modeled with an arrival angle distribution just above the wafer (doesn’t model equipment).
  \[ F_{\text{direct neutral}} + F_{\text{direct ions}} \]
  \[ F_{\text{direct}}(\theta) = F^0 \cos^n \theta \]

- The \( F_{\text{direct}} \) is the normal component of the incoming flux (which is what is needed in determining the growth rate).
  - Higher pressure systems \( \Rightarrow \) more gas phase collisions, shorter mean free path \( \Rightarrow n = 1 \) (isotropic arrival).
  - Lower pressure systems \( \Rightarrow \) fewer gas phase collisions, longer mean free path \( \Rightarrow n > 1 \) (anisotropic arrival).
  - Ionic species in biased systems \( \Rightarrow \) directed arrival \( \Rightarrow n > 1 \) (anisotropic arrival).
Considering Incoming Fluxes: Viewing Angle

- Once the direct fluxes are known, surface topography must be considered.
- Surface orientation, viewing angle and shadowing are important. Gas phase collisions are neglected near the wafer surface.
Indirect Fluxes

- The indirect fluxes are associated with processes on the wafer surface.

- Surface diffusion is driven by the local curvature of the surface (to minimize the surface free energy) and is given by

\[
F_{\text{diff net}} = F_{\text{diff net}} = \frac{D_s}{kT} \cdot \gamma' \cdot \Omega \cdot \frac{\partial^2 K}{\partial \Omega^2}
\]  

(16)

where \(D_s\) is the surface diffusivity, \(\gamma'\) is the surface energy, \(K\) is the curvature and \(\Omega\) and \(\nu\) are constants.
Surface Diffusion

- Surface diffusion helps to fill in holes, and produces more planar depositions because molecules can diffuse to "smooth out" the topography.

- $F_{\text{emitted}}^i$ arises because not all molecules "stick" when they arrive at the surface.

\[
F_{\text{emitted}}^i = (1 - S_c) F_{\text{incident}}^i
\]  \hspace{1cm} (17)

where $S_c$ is the sticking coefficient.

\[
S_c = \frac{F_{\text{reacted}}}{F_{\text{incident}}}
\]  \hspace{1cm} (18)

- Generally ions are assumed to stick ($S_c = 1$), neutrals have $S_c < 1$ and are assumed to be emitted with a cosine angle distribution (no memory of arrival angle).
Redeposited (emitted) Flux

- $F_{\text{redep (emitted)}}^{i}$ arises because the emitted flux $F_{\text{emitted}}^{i}$ can land elsewhere on the surface. Thus

$$F_{\text{redep (emitted)}}^{ik} = g_{ik}^{i} = F_{\text{emitted}}^{k} = g_{ik}^{i} = (1 - S_{ik}) F^{k}$$  \hspace{1cm} (19)

- The redeposited flux at point i due to an emitted flux at point k can then be summed over all i and k. $g_{ik}^{i}$ accounts for the geometry between i and k.

- Thus a low $S_{C} < 1$ can produce more conformal coverage because of emission/redeposition (usually more important than surface diffusion in CVD).
Sputtered Flux and Ion Flux

- The sputtered flux is caused primarily by energetic incoming ions.

\[ F_{\text{sputtered}} = Y \star \left( F_{\text{argon}} + F_{\text{direction}} \right) = Y \star F_{\text{ions}} \]

where \( Y \) is the sputtering yield. \hspace{1cm} (20)

- \( Y \) is angle sensitive which can be used to achieve more planar surfaces during deposition (example later).

- The sputtered molecules can be redeposited. This is modeled as in Eqn. (19), i.e.

\[ F_{\text{redep(sput)}} = g_{ik} \star F_{\text{sputtered}} = g_{ik} \star Y \star F_{\text{ions}} \]

\hspace{1cm} (21)

- Finally, ions striking the surface can sometime enhance the deposition rate (by supplying the energy to drive chemical reactions for example), so that

\[ F_{\text{ion-induced}} = K_{pi} \star F_{\text{ions}} \]

\hspace{1cm} (22)
Models for Different Types of Deposition Systems

- Only the typically fluxes associated with each deposition method are used in simulation.


**Stanford Profile Emulator for Etching and Deposition in IC Engineering (SPEEDIE)**

The etch and deposition simulator SPEEDIE [2] is intended to simulate two dimensional profile evolution during etching and deposition in gaseous systems. By two dimensional evolution we mean structures that can be represented by a 2D representation either because they are cylindrically symmetric or because one of their dimensions is “infinitely long,” i.e., holes (vias) or long trenches. Note that 3D particle movement is considered. The etching part of SPEEDIE is based on a previously reported etch simulator [1][6], that was completely rewritten and numerous additions were added. SPEEDIE predicts time evolution of etch profiles using physical models and parameters extracted from special test structures. The models in SPEEDIE assume:

Etch and deposition reactor pressure is below a few Torr, such that gas phase collisions within the topological features can be ignored because the mean free path is very large in comparison with the characteristic geometrical dimension of IC devices.

The fluxes for three types of species are calculated: ions, chemical radicals, and deposition precursors. Multiple transport mechanisms that are modeled include direct gas phase fluxes (1), neutral adsorption/re-emission (3), ion induced redeposition (6), surface diffusion (2), and ion reflection.
LPCVD Deposition Systems

- In these systems there are no ions involved and hence no sputtering. Surface diffusion also is usually not important.
LPCVD Deposition Systems (2)

- The sticking coefficient $S_c$ is small in these systems so there will be significant desorbed (emitted) and redeposited fluxes.
- Thus at each point on the surface,
  \[
  F_{\text{net}}^i = F_{\text{direct (neutrals)}}^i + F_{\text{redep (emitted)}}^i - (1 - S_c) \left( F_{\text{direct (neutrals)}}^i + F_{\text{redep (emitted)}}^i \right)
  = S_c \left( F_{\text{direct (neutrals)}}^i + F_{\text{redep (emitted)}}^i \right)
  = S_c \left( F_{\text{direct (neutrals)}}^i + g^i \cdot (1 - S_c) \cdot f^k \right)
  \]

- We define $\left( F_{\text{direct (neutrals)}}^i + F_{\text{redep (emitted)}}^i \right) = F_d$
  the deposition flux at each point, so the deposition rate is simply given as:
  \[
  \text{Rate} = S_c F_d / N \tag{24}
  \]
  where $N$ is the film density.
- $\cos^n \theta$ distribution is used for the incoming molecules.
PECVD Deposition Systems

- In these systems an ion flux can enhance the deposition rate by changing the surface reactions. Sputtering is usually not significant because the ion energy is low, nor is direct deposition of ions significant.

\[
F_{\text{direct(ions)}}^i \quad \text{Yes} \\
F_{\text{direct(neutals)}}^i \quad \text{No} \\
F_{\text{diff.(net)}}^i = F_{\text{diff.(in)}}^i - F_{\text{diff.(out)}}^i \quad \text{No} \\
F_{\text{emitted}}^i \quad \text{Yes} \\
F_{\text{redep(emitted)}}^i \quad \text{Yes} \\
F_{\text{sputtered}}^i \quad \text{No} \\
F_{\text{redep(sputtered)}}^i \quad \text{No} \\
F_{\text{non-induced}}^i \quad \text{Yes}
\]

- Thus

\[
\text{rate} = \frac{(S_c K_d F_i) + (K_i F_i)}{N}
\]

where \( K_d \) and \( K_i \) are relative rate constants for the neutral and ion-enhanced components respectively.
PVD Deposition Systems

- Standard PVD systems might include DC and RF sputtering systems and evaporation systems.

- Ions generally do not play a significant role in these systems, so modeling is similar to LPCVD systems.

Thus

\[
\text{rate} = \frac{S_c F_d}{N}
\]  

(26)

- The values for \( S_c \) and \( J \) would be different for LPCVD and PVD systems however.

- Sometimes these systems are operated at high temperatures, so a surface diffusion term must be added.

\[
\text{rate} = \frac{S_c F_d + \frac{D_s \gamma_s \Omega_0}{kT} \partial^2 K}{N} \partial s^2
\]  

(27)
Ionized PVD Deposition Systems

- These systems are complex to model because both ions and neutrals play a role.
- They are often used for metal deposition so that Ar\(^+\) ions in addition to Al\(^+\) or Ti\(^+\) ions may be present.
- Thus almost all the possible terms are included

\[
F_{\text{direct(neutrals)}}^{\text{F}} \\
F_{\text{direct(ions)}}^{\text{F}} \\
F_{\text{diff(nor)}}^{\text{F}} = F_{\text{diff(in)}}^{\text{F}} - F_{\text{diff(out)}}^{\text{F}} \\
F_{\text{emitted}}^{\text{F}} \\
F_{\text{sputtered}}^{\text{F}} \\
F_{\text{redeposited(emitted)}}^{\text{F}} \\
F_{\text{redeposited(sputtered)}}^{\text{F}} \\
F_{\text{ion-induced}}^{\text{F}}
\]

\[
\text{rate} = \frac{\left(S_x F_d\right) + F_i - \left(K_{sp} YF_i\right) + (K_{rd} F_{rd})}{N}
\]

where \( F_d \) includes the direct and redeposited (emitted) neutral fluxes, \( F_i \) includes the direct and ion-induced fluxes associated with the ions, and \( F_{rd} \) models redeposition due to sputtering.
High Density Plasma CVD Deposition Systems

- Very similar to IPVD (except neutral direct flux not as important):

\[
\text{rate} = \frac{(K_i F_i) - (K_{sp} YF_i) + (K_{rd} F_{rd})}{N}
\]  \hspace{1cm} (29)
### Parameter Values for Specific Systems

<table>
<thead>
<tr>
<th></th>
<th>n (exponent in cosine arrival angle distribution)</th>
<th>S_{c} (sticking coefficient)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sputter deposition</td>
<td></td>
<td></td>
</tr>
<tr>
<td>-standard</td>
<td>~1 - 4</td>
<td>~1</td>
</tr>
<tr>
<td>-ionized or collimated</td>
<td>8 - 80</td>
<td>~1</td>
</tr>
<tr>
<td>Evaporation</td>
<td>3 - 80</td>
<td>~1</td>
</tr>
<tr>
<td>LPCVD silicon dioxide</td>
<td></td>
<td></td>
</tr>
<tr>
<td>- silane</td>
<td>1</td>
<td>0.2 - 0.4</td>
</tr>
<tr>
<td>- TEOS</td>
<td>1</td>
<td>0.05 - 0.1</td>
</tr>
<tr>
<td>LPCVD tungsten</td>
<td>1</td>
<td>0.01 or less</td>
</tr>
<tr>
<td>LPCVD polysilicon</td>
<td>1</td>
<td>0.001 or less</td>
</tr>
</tbody>
</table>

- PVD systems - more vertical arrival angle distribution
  (low pressure line of sight or e field driven ions). $\therefore n > 1$ typically.
- CVD systems provide isotropic arrival angle distributions
  (higher pressure, gas phase collisions, mostly neutral molecules). $\therefore n \approx 1$ typically.
- PVD systems usually provide $S_c$ of 1. Little surface chemistry involved.
  Atoms arrive and stick.
- CVD systems involve surface chemistry and $S_c \ll 1$.
  Molecules often reemit and redeposit elsewhere before reacting.

*Therefore, CVD systems provide more conformal deposition.*
Models in SPEEDIE

**LPCVD:**
\[
\text{rate} = \frac{S_c F_d}{\text{density}} \quad \left( F_d = F_{\text{direct(neutrals)}} + F_{\text{recdep(emit)}} \right)
\]

**PECVD:**
\[
\text{rate} = \frac{(S_c K_d F_d) + (K_i F_i)}{\text{density}} \quad \left( F_i = F_{\text{ions}} \right)
\]

**Standard PVD:**
\[
\text{rate} = \frac{S_c F_d}{\text{density}}
\]

**High T PVD:**
\[
\text{rate} = \frac{S_c F_d + \frac{D_e y_s \Omega_d}{kT} \frac{\partial^2 K}{\partial s^2}}{\text{density}}
\]

**Ionized PVD:**
\[
\text{rate} = \frac{(S_c F_d) + F_i - (K_{sp} YF_i) + (K_{rd} F_{rd})}{\text{density}}
\]

**HDP CVD:**
\[
\text{rate} = \frac{(S_c K_i F_i) - (K_{sp} YF_i) + (K_{rd} F_{rd})}{\text{density}}
\]
Calibration of Models - Example: SPEEDIE

Overhang test structure allows calibration of different components

1. CVD component
2. Ion-induced deposition
3. Sputtering with angle-dependent sputter yield
4. Redeposition
5. Backscattered deposition
OVERHANG TEST STRUCTURE

BY OBSERVING DEPOSITION PROFILES IN THE CAVITY CONCLUSIONS CAN BE DRAWN ABOUT THE DEPOSITION MECHANISMS

* INFLUENCE OF CAVITY HEIGHT ON DEPOSITION ON THE UNDERSIDE
* TAPERING OF THICKNESS ON TOP SURFACE


J.P. McVittie, “Test Structure and Modeling Studies of Deposition and Etch Mechanisms”,
Talk TC1-WeM6, AVS mtg in Orlando, Florida, 1993
Topography Simulation 1 (Using SPEEDIE)

- SPEEDIE simulations for LPCVD deposition of SiO₂ with S_c = 1 (which is more typical of PVD than LPCVD) and varying values of n, the arrival angle distribution factor: (a) n=1; (c) n=10.
- Worse step coverage results as n increases (the arrival angle distribution narrows).
- Even for n = 1, conformal coverage is not achieved.

- SPEEDIE simulations for LPCVD deposition of SiO₂ in a narrow trench with the same isotropic arrival angle distribution (n=1) but different values of S_c: (a) S_c = 1; (b) S_c = 0.1; and (c) S_c = 0.01.
- Reducing S_c is much more effective than changing n if conformal deposition is desired.
Topography Simulation 2 (Using SPEEDIE)

- Results of SPEEDIE LPCVD simulations with the sidewall angle changed. $S_c = 0.2$ and $n = 1$. Note the improved trench filling.

- SPEEDIE simulations comparing LPCVD and HDPCVD depositions.
  (a) LPCVD deposition of SiO$_2$ over rectangular line. $S_c = 0.1$ and $n=1$.
  (b) HDPCVD deposition, with directed ionic flux and angle-dependent sputtering, over rectangular line showing much more planar topography.

- CMP might still be required in the HDPCVD case to fully planarize the surface.
Topography Simulation 3 (Using SPEEDIE)

- SPEEDIE simulations comparing LPCVD and HDPCVD depositions.
  (c) LPCVD deposition in trench, showing void formation. \( S_c = 0.2 \) and \( n = 1 \).
  (d) HDPCVD deposition in trench, showing much better filling.
- HDPCVD has a strong directed ion component and any overhangs that form are sputtered away.

- Actual SEM images of HDP oxide deposition.
Summary of Key Ideas

- Thin film deposition is a key technology in modern IC fabrication.
- Topography coverage issues and filling issues are very important, especially as geometries continue to decrease.
- CVD and PVD are the two principal deposition techniques.
- CVD systems generally operate at elevated temperatures and depend on chemical reactions.
- In general either mass transport of reactants to the surface or surface reactions can limit the deposition rate in CVD systems.
- In low pressure CVD systems, mass transport is usually not rate limiting.
- However even in low pressure systems, shadowing by surface topography can be important.
- In PVD systems arrival angle distribution is very important in determining surface coverage. Shadowing can be very important.
- A wide variety of systems are used in manufacturing for depositing specific thin films.
- Advanced simulation tools are becoming available, which are very useful in predicting topographic issues.
- Generally these simulators are based on physical models of mass transport and surface reactions and utilize parameters like arrival angle and sticking coefficients from direct and indirect fluxes to model local deposition rates.
Additional Notes and Simulations

- Prof. Krishna C. Saraswat, Stanford EE 311
  - [http://www.stanford.edu/class/ee311/](http://www.stanford.edu/class/ee311/)
  - See Handout 15 Deposition and Planarization Technology

- Prof. Yosi Shacham, Tel-Aviv University
  - [http://www.eng.tau.ac.il/~yosih/courses/vlsi1/](http://www.eng.tau.ac.il/~yosih/courses/vlsi1/)
  - 1 9 vacuu,.pdf
  - 1 10 cvd.pdf

- Dr. A. Doolittle, Georgia Tech ECE 6450
  - [http://users.ece.gatech.edu/~alan/index_files/ECE6450lecture.htm](http://users.ece.gatech.edu/~alan/index_files/ECE6450lecture.htm)
  - Lecture 12
  - Klecture 13 & 14
ECE 541/ME 541
Microelectronic Fabrication Techniques

MW 4:00-5:15 pm

Physical Vapor Deposition (PVD)

Zheng Yang

ERF 3017, email: yangzhen@uic.edu
Thin Film Deposition

Spin-on Films
– Polyimide (PI), photoresist (PR)
– Spin-on glass (SOG)

Physical Vapor Deposition (PVD)
– Evaporation
– Sputtering

Chemical Vapor Deposition (CVD)
– Oxidation
– LPCVD
– PECVD
Collision rates with surface.

Semiconductor fabrication is based on planar processes, so surface-gas interactions are critically important.

Number of collisions per unit time per unit area (sec\(^{-1}\) cm\(^{-2}\)):

\[ \Phi = \frac{(N/V)}{\text{v/4}} \]
\[ \Phi = \left( \frac{p}{4kT} \right) \times \sqrt{\frac{8kT}{\pi m}} \]

For \( m = 50 \text{ (amu)} \), \( T = 300^\circ\text{K} \), and \( p \) given in Torr,

\[ \Phi \sim 2.87 \times 10^{20} \text{ p collisions / (sec cm}^2\text{)} \]
Numerical examples of surface flux

<table>
<thead>
<tr>
<th>Pressure (Torr)</th>
<th>Pressure (Pa)</th>
<th>Surface flux (300°K, atomic weight= 50): molecules/(sec cm²)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1 atmosphere</td>
<td>760</td>
<td>1.01E+05</td>
</tr>
<tr>
<td>medium vacuum</td>
<td>25</td>
<td>3.30E+03</td>
</tr>
<tr>
<td>high vacuum</td>
<td>1.00E-03</td>
<td>0.113</td>
</tr>
<tr>
<td>very high vacuum</td>
<td>1.00E-06</td>
<td>1.30E-04</td>
</tr>
<tr>
<td>ultra high vacuum</td>
<td>1.00E-09</td>
<td>1.30E-07</td>
</tr>
</tbody>
</table>

Note: for Si crystal, surface atomic concentration is approximately $6.3\times10^{14}$ atoms/cm². Thus under ultra high vacuum (UHV) conditions, the surface could be contaminated in approximately 2000 seconds and in only 2 seconds in very high vacuum.
Thermal Evaporator

- Crucible containing the material to be deposited is heated.
- Good for materials with low melting point/high vapor pressure.
- Problems:
  - Heating of crucible material provides contamination.
  - Radiation from the thermal source heats the substrate.
  - Limited source size (volume) for refractive materials.
**PVD: Thermal evaporation**

Simple schematic:

- **Substrate**
- **Aperture**
- **Boat or filament**
- **To vacuum**
- **+V**
Step coverage in thermal deposition (PVD).

Planetary or perpendicular geometry.

Rotating planetary geometry.

Additional heating

Source-substrate configuration
Incident atoms
Substrates
Resulting step coverage
Deposited film
Step
Incident atoms
Heating lamps

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Rotating planetary system.

Photograph of an e-beam evaporation system with planetary substrate holder which rotates simultaneously around two axes.
Vapor pressures of some metals as function of temperature.
**Electron-beam heating.**

Thermal heating is inconvenient for evaporative deposition for several reasons:

Radiation from the thermal source heats the substrate.
Limited source size (volume) for refractive materials.

Thus electron beam heating is commonly used.

*Small well-defined region heated*
*Material serves as reservoir.*
*Minimal contaminant due to heading of crucible etc.*
*Deposition rate controlled by ebeam intensity.*
*Minimal heating to substrate.*
E-beam source

Low Cost, Compact e-beam Deposition
Practical, Low Cost, & Highly Reliable Electron Beam Deposition...

New!
Electron beam sweep controller designed for the Mighty Source™. Ultra simple & extremely effective.

MDC’s e-vap® Mighty Source™
4 Pocket Evaporation Source
State-of-the-art electronics and bullet proof reliability. 3000 watts of power, rack mountable.

MDC
Electron beam Technology
Electron beam evaporator.
Research Scale
Physical vapor deposition (PVD).

Negatives of PVD through evaporation:
  Difficult to create mixed compositions.
  Uniformity can be less than desired.
  Evaporation rates are low, throughput low.
  Dimensions required are large.
  Source is localized, can result in poor step coverage.
  Refractory materials (such as W) are difficult to evaporate.
  Non-metals are difficult.
Physical vapor deposition (PVD): Sputtering.

Improvements:
- RF plasma to maintain discharge stability, especially where insulating materials are involved.
- Magnetron for increased electron motion.
- Geometry: Large targets in proximity to substrates.

Typical schematic for RF sputtering system.
Physical vapor deposition (PVD): Sputtering.

Mechanism:
Positive ions are accelerated toward target (cathode).
Ions collide with surface at high energy, drive atoms and/or molecules off.
Ions can also exchange charge with neutral atoms which can also be accelerated toward target.
Observed angular distribution of sputtered atoms follows cosine law.
Deposition rate: 0.1-1 micron/minute.

Choice of gas:
Non-reactive -- inert gases are desirable.
Readily ionized with stable positive ions.
Reasonable cost.
Mass which matches sputtered atoms for most effective energy transfer.
Generally Argon is chosen.

Distribution of Fe atoms sputtered by normal incidence Ar⁺ ions. Fit is to cosine law.

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Step coverage in sputtering.
Typical layout for sputtering equipment.

Layout: Applied Materials Endura 5500
Physical Vapor Deposition

- No chemical reactions
- Deposition flux moves along line of sight from source to wafer.
- Cosine law applies.
- Performed in vacuum.
E-beam Evaporation

- VACUUM CHAMBER
- SUBSTRATE (DEVICE)
- ELECTRON BEAM
- CRUCIBLE (FILM MATERIAL)
Sputtering
Thermal Evaporator
Different types of thermal sources

Boats/Filaments

Crucibles/Heaters
ECE 541/ME 541
Microelectronic Fabrication Techniques

MW 4:00-5:15 pm

Chemical Vapor Deposition (CVD)

Zheng Yang

ERF 3017, email: yangzhen@uic.edu
**CVD: General considerations.**

PVD: Move material from bulk to thin film form.
- Limited primarily to metals or simple materials.
- Limited by thermal stability/vapor pressure considerations.
- Typically requires relatively high temperature and surface experiences high temperature molecules.
- Today used primarily for deposition of Al, Al:Cu, Au.
- Natural coverage: line of sight, with cos $\theta$ distribution.

CVD: Provides opportunity to deposit thin films of complex materials and in principle can be accomplished at low or modest substrate temperatures.
- Natural coverage: conformal.
- Used today primarily for dielectrics and refractory conductors.
CVD Process
Chemical reaction and typical energetics for CVD.

AB + C + (inert carrier) → A + BC + (inert carrier)
Reactions and reaction control in CVD.

Generally energy is needed to stimulate the reaction (overcome activation energy $E_A$) and to control film growth.

Thermal energy.
- CVD  normal chemical vapor deposition.
- LPCVD  low pressure CVD.
- APCVD  Atmospheric pressure CVD.
- ....

Plasma.
- PECVD  plasma enhanced CVD.
- HDPCVD  High density plasma enhanced CVD.
- RPECVD  remote plasma enhanced CVD.
- Etc...
Polysilicon CVD

SiH$_4$(gas) + H$_2$(gas) $\rightarrow$ 2H$_2$(gas) + PolySilicon (solid)

1) Mass transport of reactants
2) Film precursor reactions
3) Diffusion of gas molecules
4) Adsorption of precursors
5) Precursor diffusion into substrate
6) Surface reactions
7) Desorption of byproducts
8) By-product removal

ECE541/ME541 Microelectronic Fabrication Techniques
Film Formation during Plasma-Based CVD

1) Reactants enter chamber
2) Dissociation of reactants by electric fields
3) Film precursors are formed
4) Adsorption of precursors
5) Precursor diffusion into substrate
6) Surface reactions
7) Desorption of by-products
8) By-product removal

Same as CVD, but plasma accelerates reactions; charged products deposit anisotropically; and extra energy in products increases the final film quality.

ECE541/ME541 Microelectronic Fabrication Techniques
Some exemplary data for deposition of polysilicon:

High temperature: deposition limited by mass transport

Low temperature: deposition limited by chemical reaction

° SiH₄
+ SiH₂Cl₂
△ SiHCl₃
□ SiCl₄
A different way to plot the growth rate:
CVD Reactor designs – examples.

Horizontal flow reactors, (a) and (b).

Pancake reactor (c), and barrel reactor (d).

Single wafer reactors, (e) and (f).
Plasma Enhanced CVD Processing System

Process chamber
Gas inlet
Capacitive-coupled RF input
Chemical vapor deposition
Wafer
Susceptor
Exhaust
Heat lamps

CVD cluster tool

Figure 9.7

ECE541/ME541 Microelectronic Fabrication Techniques
Page 11
High Density Plasma Deposition Chamber

- Popular since ~ 1995
- High density plasma
- Highly directional due to wafer bias
- **Fills** high aspect ratio gaps (**deposition mode**)
- Backside He cooling to relieve high thermal load
- Simultaneously deposits and etches film to prevent bread-loaf and key-hole effects

*Photograph courtesy of Applied Materials, Ultima HDPCVD Centura*
**Typical deposition conditions and properties of silicon oxide films deposited using HDP CVD.**

<table>
<thead>
<tr>
<th>Process parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Source rf power</td>
<td>2000-4000 W</td>
</tr>
<tr>
<td>Gases</td>
<td>SiH$_4$/Ar/O$_2$ = 32-45/0-40/43-60 sccm.</td>
</tr>
<tr>
<td>Pressure</td>
<td>&lt;5 mTorr</td>
</tr>
<tr>
<td>Deposition/sputtered ratio</td>
<td>3.2:1 (filled 0.25 μm, 2.5:1 aspect ratio).</td>
</tr>
<tr>
<td>Deposition temperature</td>
<td>250-350°C</td>
</tr>
<tr>
<td>Deposition rate</td>
<td>180-400 nm/min</td>
</tr>
<tr>
<td>Refractive index</td>
<td>1.46 ± 0.003</td>
</tr>
<tr>
<td>Film stress (0.7 μm, 25°C)</td>
<td>(-)1.0-1.6 x 10$^9$ dynes/cm$^2$.</td>
</tr>
<tr>
<td>Wet-etching (6:1 buffered HF)</td>
<td>1.6-1.8 x that of thermal oxide.</td>
</tr>
</tbody>
</table>
Step coverage variation with process.

Films of silicate glass deposited on 0.3 micron features.

Conformal coverage of LPCVD process based on TEOS.

“Bread-loaf” profile of PECVD process based on TEOS.

Unique profile of HDP CVD process based on silane.


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Polysilicon or polycrystalline silicon deposition.

Uses: primarily as conductive material.
  - Conductor in CMOS, bipolar, and related structures.
  - Resistors.
  - Electrodes for internal capacitors (DRAM for example).

Advantages:
  - Compatible with silicon.
  - Withstands subsequent high temperature processing.
  - Excellent interface with SiO₂ (low defect density etc.).
  - Conformal coverage.

A layer of polysilicon is then deposited onto the silicon dioxide surface using chemical vapor deposition. This material will serve as the transistor's gate.
Polysilicon silicon deposition

Primary basic chemistry:

\[ \text{SiH}_4 \rightarrow \text{Si} + 2\text{H}_2 \]


Pressure \( \sim 0.3\text{-}1.0 \) torr.

\[ T_{\text{reaction}} \sim 580^\circ - 650^\circ \text{C.} \]

Lower temperatures give too slow reaction. Higher temperatures give rise to gas phase reaction (particulates).

Deposition rate in realm of 0.01 micron/min.

Deposition time approx. 2.5 hours for 0.3 micron film.
Silicon dioxide and related dielectric material deposition

Uses:

- Gate dielectric (MOS, CMOS etc.)
- Isolation of internal transistor from metal conductor.
- Outer metallization insulation.
- Storage of charge – capacitance (EPROM).
- Passivation layers.
- Dopant Diffusion sources.
- Diffusion and implantation masks.

Structure generally amorphous with SiO$_2$ in local tetrahedral configuration.

Sometimes referred to as USG for undoped silicate glass.
Silicon dioxide deposition.

Basic chemistry: low temperature silane process.

\[ \text{SiH}_4 + \text{O}_2 \text{ (nitrogen carrier)} \rightarrow \text{SiO}_2 + 2\text{H}_2 \]

*Pressure* \(\sim\) \(<1\) atmosphere; *silane partial pressure in realm of 1 torr; oxygen in excess.*

*\(T_{\text{reaction}}\) ~ 310° – 450° C.*

*Activation energy approx. 0.4 eV.*

*Films slightly porous, densification at 700°-1000° C necessary for high quality films.*

Film quality measurements:

<table>
<thead>
<tr>
<th>Property</th>
<th>Low T silane</th>
<th>Thermal oxide</th>
</tr>
</thead>
<tbody>
<tr>
<td>Dielectric constant</td>
<td>3.2-3.4</td>
<td>3.9</td>
</tr>
<tr>
<td>Refractive index</td>
<td>1.44</td>
<td>1.46</td>
</tr>
<tr>
<td>Etch rate*</td>
<td>3 - &gt;10</td>
<td>(1.0)</td>
</tr>
</tbody>
</table>

*Slightly Porous*
Silicon dioxide deposition

Basic chemistry: low temperature plasma enhanced process.

\[
\text{SiH}_4 + 2\text{N}_2\text{O} \text{ (argon carrier)} \rightarrow \text{SiO}_2 + 2\text{H}_2 + 2\text{N}_2
\]

Pressure \(\sim\) .

\(T_{\text{reaction}} \sim 200^\circ - 400^\circ\text{C.}\)

Activation energy approx. 0.4 eV.

Films slightly porous, densification at 700\(^\circ\)-1000\(^\circ\text{C}\) necessary for high quality films.

<table>
<thead>
<tr>
<th>Property</th>
<th>Low (T) PECVD</th>
<th>Thermal oxide</th>
</tr>
</thead>
<tbody>
<tr>
<td>Slightly Silicon Rich</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Dielectric constant</td>
<td>4-5</td>
<td>3.9</td>
</tr>
<tr>
<td>Refractive index</td>
<td>(\sim 1.46)</td>
<td>1.46</td>
</tr>
<tr>
<td>Etch rate*</td>
<td>(\sim 2-10)</td>
<td>(1.0)</td>
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<tr>
<td>Dielectric strength</td>
<td>4-8 MV/cm</td>
<td>12-15 MV/cm</td>
</tr>
</tbody>
</table>

ECE541/ME541 Microelectronic Fabrication Techniques
**Silicon dioxide deposition**

Basic chemistry: TEOS (tetraethyl orthosilicate) process.  
\[ \text{Si(OCH}_2\text{CH}_3)_4 \text{ (nitrogen carrier)} \rightarrow \text{SiO}_2 + 4\text{C}_2\text{H}_4 + 2\text{H}_2\text{O} \]

*TEOS is stored as liquid (but used as gas phase reactant).*

Conventional CVD (medium temperature) process.  
Impurities present such as C – add O\(_2\) to minimize.  
\( T_{\text{reaction}} \) 680-730\(^\circ\)C (cannot be used over Al).  
0.03 micron/minute deposition rate.  
Improved step coverage relative to silane process.

PE CVD (low temperature) process.  
\( T_{\text{reaction}} \) 250-425\(^\circ\)C.  
Total pressure 2-10 torr.  
0.1 micron/minute deposition rate.
**CVD Silicon Nitride Deposition.**

Uses:
- Final passivation and mechanical protection.
- Mask for selective oxidation of Si.
- Charge storage dielectric in MOS capacitors.
- Sidewall structures in MOSFETs.
- CMP stop-layer.

Basic chemistry: low pressure CVD process.

\[ 3\text{SiCl}_2\text{H}_2 + 4\text{NH}_3 \text{ (carrier)} \rightarrow \text{Si}_3\text{N}_4 + 6\text{H}_2 + 6\text{HCl} \]

- \( T_{\text{reaction}} \sim 700^\circ \text{C} - 800^\circ \text{C} \)
- Deposition rate 0.01 micron/min.

Basic chemistry: Plasma enhanced CVD process.

\[ \text{SiH}_4 + \text{NH}_3 \rightarrow \text{Si}_x\text{N}_y\text{H}_z + \text{H}_2 \]

- \( T_{\text{reaction}} \sim 200^\circ \text{C} - 400^\circ \text{C} \)
- \( P=0.2-0.3 \text{ torr} \)
- Deposition rate 0.05 micron/min.
Other useful CVD deposition processes:

**WSi₂: Tungsten Silicide.**

Uses:
- Local interconnect (bit lines in memory devices).
- Adhesion layers (for W for example).

\[
WF_6 + 2\ SiH_4 \rightarrow WSi_2 + 6\ HF + H_2 \quad (300-400^\circ C, \text{low pressure})
\]

\[
2WF_6 + 7SiH_2Cl_2 \rightarrow 2WSi_2 + 3SiCl_4 + 12HF + 2HCl \quad (600^\circ C)
\]

**TiN: Titanium nitride.**

Refractory (2950^\circ C) with relatively low resistivity (50\( \mu \Omega\)-cm)
Uses:
- Diffusion barriers (for Cu for example).
- Adhesion layers.

\[
6\ TiCl_4 + 8\ NH_3 \rightarrow 6\ TiN + 24\ HCl + N_2 \quad (600^\circ C, \text{low pressure})
\]
**CVD W (tungsten) Deposition**

Uses:
- Metal vias ("plug").
- Local metallization.

Basic chemistries:

\[ 2 \text{WF}_6 + 3 \text{Si} \rightarrow 2 \text{W} + 3 \text{SiF}_4 \]  

(300°C, 0.015 micron)

\[ \text{WF}_6 + 3 \text{H}_2 \rightarrow \text{W} + 6 \text{HF} \]  

(low pressure, 450°C)

\[ 2 \text{WF}_6 + 3 \text{SiH}_4 \rightarrow 2 \text{W} + 3 \text{SiF}_4 + 6 \text{H}_2 \]  

(low pressure, 300°C)
<table>
<thead>
<tr>
<th>Product</th>
<th>Reactants</th>
<th>Method</th>
<th>Temperature (°C)</th>
<th>Comments</th>
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<tbody>
<tr>
<td>Poly-silicon</td>
<td>SiH₄</td>
<td>LPCVD</td>
<td>580 – 650</td>
<td>May be in situ doped</td>
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<tr>
<td>Silicon Nitride</td>
<td>SiH₄ + NH₃</td>
<td>LPCVD</td>
<td>700 – 900</td>
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<td></td>
<td>SiC₁₂H₂ + NH₃</td>
<td>LPCVD</td>
<td>650 – 750</td>
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<td></td>
<td>SiH₄ + NH₃</td>
<td>PECVD</td>
<td>200 – 350</td>
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<tr>
<td></td>
<td>SiH₄ + N</td>
<td>PECVD</td>
<td>200 – 350</td>
<td></td>
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<tr>
<td>SiO₂</td>
<td>SiH₄ + O₂</td>
<td>APCVD</td>
<td>300 – 500</td>
<td>Poor step coverage</td>
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<tr>
<td></td>
<td>SiH₄ + O₂</td>
<td>PECVD</td>
<td>200 – 350</td>
<td>Good step coverage</td>
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<tr>
<td></td>
<td>SiH₄ + N₂O</td>
<td>PECVD</td>
<td>200 – 350</td>
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<tr>
<td>Si(O₂C₂H₅)₄[TEOS]</td>
<td>LPCVD</td>
<td>650 – 750</td>
<td>Liquid source, conformal</td>
<td></td>
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<tr>
<td>SiC₁₂H₂ + N₂O</td>
<td>LPCVD</td>
<td>850 – 900</td>
<td>conformal</td>
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<tr>
<td>Doped SiO₂</td>
<td>SiH₄ + O₂ + PH₃</td>
<td>APCVD</td>
<td>300 – 500</td>
<td>PSG</td>
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<td>SiH₄ + O₂ + PH₃</td>
<td>PECVD</td>
<td>300 – 500</td>
<td>PGS</td>
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<tr>
<td></td>
<td>SiH₄ + O₂ + PH₃ + B₂H₆</td>
<td>APCVD</td>
<td>300 – 500</td>
<td>BPSG, low temperature flow</td>
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<tr>
<td></td>
<td>SiH₄ + O₂ + PH₃ + B₂H₆</td>
<td>PECVD</td>
<td>300 – 500</td>
<td>BPSG, low temperature flow</td>
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ECE 541/ME 541
Microelectronic Fabrication Techniques

MW 4:00-5:15 pm

Atomic Layer Deposition (ALD)

Zheng Yang

ERF 3017, email: yangzhen@uic.edu
What is ALD?

• Atomic Layer Deposition  
  a.k.a. Molecular Layering (Rus.) Molecular Layer Epitaxy, ALE (Atomic Layer Epitaxy)  
  ALG (Atomic Layer Growth), etc…
• In essence, a pulsed form of thermal CVD
• Slow.
• Growth is controlled by total available precursor on surface, rather than precursor flux and reactivity, as in “regular” CVD.
• Invented by Russian researchers in 1960’s, independently by Finns in 1970’s.
• Very Slow
What about “regular” CVD

- In standard CVD deposition, typically two or more reactants are flowed over a surface, under vacuum, with either thermal or plasma excitation, or both.
- Reactants land on surfaces, scitter around, bump into each other, and react, on a continuous basis.
- Local reaction rate is function of temperature, pressure, reactant flux (gas flow, local plasma density, chamber geometry, surface morphology and aspect ratio, phase of moon…), pump rate, local cooling rate, bias voltage, value of product, etc.
- i.e. Many Variables must be managed
What about “regular” CVD (cont.)

- In standard CVD deposition, deposition rates can range between 1000-10,000A (1 um)/min.
- Film quality is generally good, but can be porous, less dense than in other techniques, somewhat less smooth. Conformality better than sputtering and evaporation, but limited to aspect ratios of less than ~3-5.
- Oxides sometimes require annealing.
What about ALD?…

- In ALD, reactants/precursors are introduced in alternating pulses, rather than concurrently.
- First precursor is pulsed into reactor, lands on surfaces, and forms a "monolayer", which remains as excess precursor is purged from reactor and pumped away.
- Second precursor is pulsed into reactor, lands on surfaces, and reacts with first monolayer, to completion, so that first monolayer is consumed.
- Growth cycle is complete, leaving ~1 angstrom of material. Cycle is repeated…several times.
What about ALD? (cont.)...

- Because reactions are allowed to go to completion, and growth during a cycle is controlled by the total reactant present rather than a flux of reactant, growth/cycle is independent of almost all variables, and only depends on sufficient precursor to cover area of interest, temperature sufficient to allow reaction to proceed, and time sufficient for each layer to react to completion.
- Exceedingly simple to control. No process MFCs, no tuning networks, no pressure controllers, no sophisticated power supplies, no process cooling, etc.
- Exceedingly high conformality, aspect ratios from 100s to 100,000 demonstrated.
- Excellent uniformity over 8" sample, ± 1%
- Very Slow. (~6 Å/min)
Chemical Vapor Deposition (CVD)

One or more gases or vapors react to form a solid product

Solid product can be a
film
particle
nanowire
nanotube

Reaction started by
heat
mixing 2 vapors
plasma
Atomic Layer Deposition (ALD)

Sequential, self-limiting surface reactions make alternating layers:

Benefits of ALD:

- Atomic level of control over film composition ⇒ nanolaminates and multi-component materials
- Uniform thickness over large areas and inside narrow holes
- Very smooth surfaces (for amorphous films)
- High density and few defects or pinholes
- Low deposition temperatures (for very reactive precursors)
- Pure films (for suitably reactive precursors)
ALD Cycle for Al₂O₃ Deposition

In air H₂O vapor is adsorbed on most surfaces, forming a hydroxyl group. With silicon this forms: Si-O-H₃⁻. After placing the substrate in the reactor, Trimethyl Aluminum (TMA) is pulsed into the reaction chamber.

- Trimethyl Aluminum (TMA) reacts with the adsorbed hydroxyl groups, producing methane as the reaction product.

\[
\text{Al(CH₃)₃(g)} + \text{Si-O-H₃⁻} \rightarrow \text{Si-O-Al(CH₃)₂} + \text{CH₄}
\]
ALD Cycle for Al₂O₃ Deposition

- Trimethyl Aluminum (TMA) reacts with the adsorbed hydroxyl groups, producing methane as the reaction product.

\[ \text{Al(CH₃)₃}_{(g)} + : \text{Si-O-H}_{(s)} \rightarrow \text{Si-O-Al(CH₃)₃}_{(s)} + \text{CH}_₄ \]
ALD Cycle for Al₂O₃ Deposition

- Trimethyl Aluminum (TMA) reacts with the adsorbed hydroxyl groups, until the surface is passivated. TMA does not react with itself, terminating the reaction to one layer. This causes the perfect uniformity of ALD. The excess TMA is pumped away with the methane reaction product.
After the TMA and methane reaction product is pumped away, water vapor (H₂O) is pulsed into the reaction chamber.
ALD Cycle for $\text{Al}_2\text{O}_3$ Deposition

- $\text{H}_2\text{O}$ reacts with the dangling methyl groups on the new surface forming aluminum-oxygen (Al-O) bridges and hydroxyl surface groups, waiting for a new TMA pulse. Again, methane is the reaction product.

\[
2 \text{H}_2\text{O} (g) + \text{Si-O-Al(CH}_3)_2 (s) \rightarrow \text{Si-O-Al(OH)}_2 (s) + 2 \text{CH}_4
\]
ALD Cycle for Al₂O₃ Deposition

- The reaction product methane is pumped away. Excess H₂O vapor does not react with the hydroxyl surface groups, again causing perfect passivation to one atomic layer.
ALD Cycle for Al$_2$O$_3$ Deposition

- One TMA and one H$_2$O vapor pulse form one cycle. Here three cycles are shown, with approximately 1 Angstrom per cycle. Each cycle including pulsing and pumping takes, e.g. 3 sec.

Two reaction steps in each cycle:

\[
\text{Al(CH$_3$_2)$_3$(s)} + :\text{Al-O-H}(s) \rightarrow :\text{Al-O-Al(CH$_3$_2)$_2$(s)} + \text{CH}_4
\]

\[
2 \text{H}_2\text{O}(g) + :\text{O-Al(CH$_3$_2)$_2$(s)} \rightarrow :\text{Al-O-Al(OH)$_2$(s)} + 2 \text{CH}_4
\]
Cambridge Nanotech Savannah 200 ALD

ECE541/ME541 Microelectronic Fabrication Techniques
Savannah 200 Hardware

Sample Chamber (8" capable)
Precursor manifold (N2 purged)
ALD valves
Pressure gauge
Precursor cylinders
Vacuum valve ("Stop Valve")
Vacuum pump (not shown)
Savannah 200 Software—Overview
Savannah 200 Software—Parameters

<table>
<thead>
<tr>
<th>Instruction #</th>
<th>value</th>
</tr>
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<tr>
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</tr>
<tr>
<td>1</td>
<td>heater</td>
</tr>
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<td>heater</td>
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<td>3</td>
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<td>4</td>
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<tr>
<td>5</td>
<td>wait</td>
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<tr>
<td>6</td>
<td>pulse</td>
</tr>
<tr>
<td>7</td>
<td>wait</td>
</tr>
<tr>
<td>8</td>
<td>goto</td>
</tr>
<tr>
<td>9</td>
<td>wait</td>
</tr>
</tbody>
</table>
Savannah 200 Pressure Monitoring

- No pressure control – monitoring only
Temperatures are set in recipe, or in manual control boxes.

Oxide processes are fairly insensitive to temperature, but chamber and manifold setpoints must be kept above precursor temps., or...
Savannah 200
Precursor Pulse Control

- Pulse times are set in recipe. They need to be of a minimum time, to ensure complete coverage of reactor and sample.
- 15 mS is sufficient for high-vapor-pressure precursors (Trimethyl Aluminum, H2O)
- Lower vapor pressure materials (Cu, Pt precursors) need to be maintained at higher temperatures (80-150C) to produce sufficient vapor pressure, and use longer pulse times to cover the reactor.
• "Too short" pulses can lead to insufficient area coverage.

Pt deposition within coverage zone is full thickness, due to self-limiting nature of reaction, (not subject to variations in vapor pressure)

Can be used to create a "virtual" reaction chamber of smaller size, conserving expensive precursor
Savannah 200
Other controls

- Precursor manifold configuration
- N2 flow manual setting
- Process monitoring:
  Cycles remaining
  Time remaining
Advantages of ALD

- Due to exceedingly high conformality, very high aspect ratio structures can be coated, including the insides of microfluidic devices and micro-porous structures.
- Due to astounding process stability, repeatability and film quality is excellent.
- Due to the insensitivity to process variables and self-limiting growth steps, absurdly high-uniformity is achievable.
- Inherently high uniformity allows batch processing; samples or wafers can be run in large chambers, allowing multiple cassettes to be run simultaneously (similar to tube furnaces).
- Low temperature deposition of high quality films allows processing of previously unworkable substrate types.
Filling larger aspect-ratio Holes with ALD

Aspect Ratio ~50:1

4 cycles 12 cycles

Acknowledge to Dr. Gordon at Harvard

ECE541/ME541 Microelectronic Fabrication Techniques
Coatings on the Outside of Particles

ALD AlN coating

ZnS particles

Used in electroluminescent back-lights for displays in cell-phones and many other devices.

Acknowledgment to Dr. Gordon at Harvard
Photonic Crystals by ALD

1) Form crystals of silica spheres.
2) ALD of Ta$_2$O$_5$ between the spheres
3) Convert to Ta$_3$N$_5$ in NH$_3$
4) Dissolve the silica spheres in HF

Acknowledge to Dr. Gordon at Harvard
Nano-Dots by ALD

ALD ruthenium on aluminum oxide

diameters ~1 to 2 nm,
~ 5 to 10 atoms across

nucleation density is
~ 20 x higher than previous metal nanocrystals

may be applied to flash memories 40 nm scale bar; 10 nm in insert

Acknowledgment to Dr. Gordon at Harvard
Alumina Nanotubes on Carbon Nanotubes

7 nm diameter  21 nm diameter  100 nm diameter

Acknowledgement to Dr. Gordon at Harvard

ECE541/ME541 Microelectronic Fabrication Techniques

Page 30
Nano-Coaxial Cable or Transistor

Conducting tungsten nitride (WN) concentrically around insulating aluminum oxide (Al₂O₃) concentrically around a conducting carbon nanotube.

WN  Al₂O₃  Carbon  Al₂O₃  WN

Acknowledgment to Dr. Gordon at Harvard
ALD Al$_2$O$_3$ – 450 cycles 6" wafer on Gaertner Laser Ellipsometer

- Thickness
  Unif. –
  0.84 %
Yet more ALD Deposition Advantages…

- Thickness determined simply by number of cycles
- Very smooth, dense, pin-hole free films
- Precursors are saturatively chemisorbed => stoichiometric films with large area uniformity and 3D conformality
- Nanolaminates and mixed oxides possible
- Low temperature deposition possible (Room Temp. - 400 °C)
- Gentle deposition process for sensitive substrates
ALD Deposition Disadvantages

- Slow
- High conformality means even back-side of sample gets deposition – sometimes a problem.
- Masking not effective for all films
- Some films are quite substrate sensitive, and even "atmosphere" sensitive.
- Lift-off processing possible, but not optimal due to high conformality.

- Very Slow
What Materials are available using ALD?

- Many Oxides, with excellent film qualities, most popularly – Al₂O₃, HfO₂, SiO₂, LaO₂, TiO₂
- Several metals and pure elements - Pt, Cu, Si, Ge, Sb.
- Nitrides.
- Rare-Earth Oxides.
Current Applications of ALD
Electroluminescent displays (Al₂O₃, AlN, ZnS)
Read/Write heads in magnetic disk storage (Al₂O₃)
Insulators in capacitors in DRAMs (Al₂O₃, HfO₂)
Insulation and spacer layers in microelectronics (SiO₂, Si₃N₄)
Metal/insulator in transistor gates (TaN/HfO₂)
Planar waveguides and optical filters (SiO₂, TiO₂)

 Likely Future Applications of ALD
Insulators in microelectronic capacitors (Ta₂O₅, SrTiO₃, LaLuO₃)
Diffusion barriers for copper in interconnects (WN, TaN, Mn)
Adhesion and seed layers for interconnects (Co₄N, Ru, Cu)
Sealing pores in low-k dielectrics (SiO₂)
Magnetic disk storage (Al₂O₃, Fe, Co, Ni, Cu, Ru, Mn, Pt)
Nano-Electronics
Catalysts . . .
Elements included in ALD Materials

Green = Element included in at least 1 ALD Material

Red = Element not included in any ALD Material

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<tbody>
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Pure Elements Made by ALD

Green = ALD processes known for 16 Pure Elements

Red = no process known for ALD of the Element

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</table>
Nitrides Made by ALD

Green = ALD processes known for a Nitride of the Element

Red = no process known for ALD of a Nitride of the Element

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<td>Gd</td>
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<td></td>
<td>Tb</td>
<td>Dy</td>
<td>Ho</td>
<td>Er</td>
<td>Tm</td>
<td>Yb</td>
<td>Lu</td>
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<tr>
<td></td>
<td></td>
<td></td>
<td>Th</td>
<td>Pa</td>
<td>U</td>
<td></td>
<td></td>
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</tr>
</tbody>
</table>
Sulfides Made by ALD

Green = ALD processes known for a Sulfide of the Element

Red = no process known for ALD of a Sulfide of the Element

H Li Be B C N O F Ne
Li Na Mg Al Si P S Cl Ar
K Ca Sc Ti V Cr Mn Fe Co Ni Cu Zn Ga Ge As Se Br Kr
Rb Sr Y Zr Nb Mo Tc Ru Rh Pd Ag Cd In Sn Sb Te I Xe
Cs Ba La Hf Ta W Re Os Ir Pt Au Hg TI Pb Bi Po At Rn
Fr Ra Ac Ce Pr Nd Pm Sm Eu Gd Tb Dy Ho Er Tm Yb Lu
Th Pa U Np Pu Am Cm Bk Cf Es Fm Md No Lr
Carbides Made by ALD

Green = ALD processes known for a Carbide of the Element

Red = no process known for ALD of a Carbide of the Element

H He
Li Be
Na Mg
K Ca Sc Ti V Cr Mn Fe Co Ni Cu Zn Ga Ge As Se Br Kr
Rb Sr Y Zr Nb Mo Tc Ru Rh Pd Ag Cd In Sn Sb Te I Xe
Cs Ba La Hf Ta W Re Os Ir Pt Au Hg Ti Pb Bi Po At Rn
Fr Ra Ac
Ce Pr Nd Pm Sm Eu Gd Tb Dy Ho Er Tm Yb Lu
Th Pa U Np Pu Am Cm Bk Cf Es Fm Md No Lr
Fluorides Made by ALD

Green = ALD processes known for a Fluoride of the Element
Red = no process known for ALD of a Fluoride of the Element

H Li Be Na K Rb Cs Fr He
Li Be Mg Ca Sr Ba Ra
V Cr Mn Fe Tc W Re Ta Hf
Mn Cr Fe Co Ni Cu Zn Yb
Ti V Cr Mn Fe Co Ni Cu Zn
Al Si P S Cl Ar Ga Ge Sn Sb Te I
B C N O F Ne Al Si P S Cl Ar
Ga Ge As Se Br Kr
Zr Nb Mo Tc Ru Rh Pd Ag Cd In Sn Sb Te I Xe
Cs La Hf Ta W Re Os Ir Pt Au Hg Tl Pb Bi Po At Rn
Ce Pr Nd Pm Sm Eu Gd Tb Dy Ho Er Tm Yb Lu
Th Pa U Np Pu Am Cm Bk Cf Es Fm Md No Lr

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### Frequently used depositions by ALD

<table>
<thead>
<tr>
<th>ALD Film</th>
<th>Dep. Temp.</th>
<th>Second Precursor</th>
<th>Notes</th>
</tr>
</thead>
<tbody>
<tr>
<td>Al$_2$O$_3$</td>
<td>Room temp. to 300C</td>
<td>H$_2$O</td>
<td>Precursor (TMA) is pyrophoric- spontaneously burns (brightly) in air.</td>
</tr>
<tr>
<td>HfO$_2$</td>
<td>120-250C</td>
<td>H$_2$O</td>
<td></td>
</tr>
<tr>
<td>SiO$_2$</td>
<td>130-250C</td>
<td>TMA+ H$_2$O</td>
<td>Not &quot;pure&quot; ALD process, uses Al2O3 layer for catalysis of silanol</td>
</tr>
<tr>
<td>Pt</td>
<td>270C</td>
<td>H$_2$</td>
<td>Doesn't like polymer, Prec. Very Expensive</td>
</tr>
<tr>
<td>ALD Film</td>
<td>Dep./Cycle</td>
<td>Ref. Index</td>
<td>Dielectric Constant ((\varepsilon))</td>
</tr>
<tr>
<td>----------</td>
<td>------------</td>
<td>------------</td>
<td>--------------------------------------</td>
</tr>
<tr>
<td>Al(_2)O(_3)</td>
<td>1.1 Å</td>
<td>1.65</td>
<td>10.8</td>
</tr>
<tr>
<td>HfO(_2)</td>
<td>0.95 Å</td>
<td>2.05</td>
<td>18.0</td>
</tr>
<tr>
<td>SiO(_2)</td>
<td>15-20 Å</td>
<td>1.46</td>
<td></td>
</tr>
<tr>
<td>Pt</td>
<td>0.48 Å</td>
<td>12.15 uΩ·cm</td>
<td>10.60 uΩ·cm</td>
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</tbody>
</table>

Sheet resistivity for comparison
ALD Oxide Characterization

• Best suited to ellipsometry
• Initial process qualification using Woollam spectroscopic ellipsometer - Slow, very precise
• Sustaining characterization can use laser ellipsometer – single wavelength, fast, requires some knowledge of film.
Some leakage current values

![Leakage current values graph](image_url)

**Acknowledgement to Dr. Gordon at Harvard**

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