EE C247B – ME C218
Introduction to MEMS Design
Spring 2016
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Lecture Module 3: Oxidation & Film Deposition

Lecture Outline

• Reading: Senturia, Chpt. 3; Jaeger, Chpt. 2, 3, 6
  ◊ Example MEMS fabrication processes
  ◊ Oxidation
  ◊ Film Deposition
    ◆ Evaporation
    ◆ Sputter deposition
    ◆ Chemical vapor deposition (CVD)
    ◆ Plasma enhanced chemical vapor deposition (PECVD)
    ◆ Epitaxy
    ◆ Atomic layer deposition (ALD)
    ◆ Electroplating
Making Mechanical Devices

• How best does one make a mechanical product?
• Assembly line production?
  - Pick and place parts
  - Used for many macroscopic mechanical products
  - Robotic automation greatly reduces cost
• Problem: difficult to do this with MEMS-scale parts (but not impossible, as we’ll soon see …)
• Solution: borrow from integrated circuit (IC) transistor technology
  - Use monolithic wafer-level fabrication methods
  - Harness IC’s batch methods, where multiple devices are achieved all at once
Polysilicon Surface-Micromachining

- Uses IC fabrication instrumentation exclusively
- Variations: sacrificial layer thickness, fine vs. large-grained polysilicon, in situ vs. POCl₃-doping

Silicon Substrate

Hydrofluoric Acid Release Etchant

Free-Standing Polysilicon Beam

300 kHz Folded-Beam Micromechanical Resonator

Electroplating: Metal MEMS

- Use electroplating to obtain metal μstructures
- When thick: call it “LIGA”
- Pros: fast low temp deposition, very conductive
- Cons: drift, low mech. Q but may be solvable?
**Bulk Micromachining and Bonding**

- Use the wafer itself as the structural material
- Adv: very large aspect ratios, thick structures
- Example: deep etching and wafer bonding

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**Oxidation**

[Diagram of Micromechanical Vibrating Ring Gyroscope]
Thermal Oxidation of Silicon

* Achieved by heating the silicon wafer to a high temperature (~900°C to 1200°C) in an atmosphere containing pure oxygen or water vapor

* Enabling reactions:

For dry oxygen:

\[ \text{Si} + \text{O}_2 \rightarrow \text{SiO}_2 \]

For water vapor:

\[ \text{Si} + 2\text{H}_2\text{O} \rightarrow \text{SiO}_2 + 2\text{H}_2 \]

Schematically:

High T (~900°C – 1200°C)

In dry O\(_2\) or Water vapor

Oxidation Modeling

(1) Initially: (no oxide @ surface)

\begin{align*}
\text{gas stream} & \rightarrow \text{Si} \\
& \quad \text{Growth rate determined by reaction rate @ the surface}
\end{align*}

(2) As oxide builds up:

\begin{align*}
\text{gas stream} & \rightarrow \text{oxide} \rightarrow \text{Si} \\
& \quad \text{Reactant must diffuse to Si surface where the oxidation reaction takes place} \\
& \quad \text{Growth rate governed more by rate of diffusion to the silicon-oxide interface}
\end{align*}
Oxidation Modeling (cont.)

At the Si-SiO₂ interface:
Oxidation rate \( \propto N_i \) \( \Rightarrow \) J \( \propto N_i \) \( \Rightarrow \) J = \( k_i N_i \) \( \text{(2)} \)

Combining (1) and (2):

\[
N_i = \frac{J}{k_i} \Rightarrow J = D \left( \frac{N_o - J/k_i}{X_{ox}} \right)
\]

\[
JX_{ox} = DN_o - \frac{DJ}{k_i} \Rightarrow J \left( X_{ox} + \frac{D}{k_i} \right) = DN_o
\]

\[
\therefore J = \frac{DN_o}{X_{ox} + \frac{D}{k_i}} = \text{Flux of reactants}
\]
Oxidation Modeling (cont.)

Find an expression for \( X_{OX}(t) \):

\[
\frac{dX_{OX}}{dt} = \frac{J}{M} = \frac{DN_{O}/M}{X_{OX} + D/k_s} \tag{3}
\]

Rate of change of oxide layer thickness w/time

oxidizing flux

\# of molecules of oxidizing species incorporated into a unit volume of oxide

\[
= 2.2 \times 10^{22} \text{cm}^{-3} \quad \text{for O}_2
\]

\[
= 4.4 \times 10^{22} \text{cm}^{-3} \quad \text{for H}_2\text{O}
\]

Solve (3) for \( X_{OX}(t) \):

[Initial condition \( X_{OX}(t = 0) = X_i \)]

\[
\frac{dX_{OX}}{dt} = \frac{DN_{O}/M}{X_{OX} + D/k_s} \overset{X_{OX}}{\int} \left( X_{OX} + \frac{D}{k_s} \right) dX_{OX} = \int_{0}^{t} \frac{DN_{O}}{M} \, dt
\]

Oxide Thickness Versus Time

Result:

\[
X_{OX}(t) = \frac{A}{2} \left\{ 1 + \frac{4B}{A^2} \left( t + \tau \right)^{1/2} \right\} - 1
\]

where

\[
A = \frac{2D}{k_s} \\
B = \frac{2DN_{O}}{M} \\
\tau = \frac{X_i^2}{B} + \frac{X_i}{(B/A)}
\]

\[
D = D_0 \exp \left( -\frac{E_A}{kT} \right)
\]

additional time required to go from \( X_i \rightarrow X_{OX} \)

time required to grow \( X_i \) \[X_i = \text{initial oxide thickness}\]

\( i.e. \), \( D \) governed by an Arrhenius relationship \( \rightarrow \) temperature dependent
Oxidation Modeling (cont.)

For shorter times:

\[
(t + \tau) \ll \frac{A^2}{4B} \Rightarrow X_{OX}(t) = \left( \frac{B}{A} \right)(t + \tau)
\]

oxide growth limited by reaction at the Si-SiO\(_2\) interface

Taylor expansion (first term after 1's cancel)

linear growth rate constant

For long oxidation times: oxide growth diffusion-limited

\[
(t + \tau) \gg \frac{A^2}{4B} \Rightarrow X_{OX}(t) = \sqrt{B(t + \tau)} \approx \sqrt{Bt}
\]

\(t \gg \tau\)

Parabolic rate constant

Oxidation Rate Constants

<table>
<thead>
<tr>
<th>Ambient</th>
<th>(C_1)</th>
<th>B/A</th>
<th>(C_2)</th>
<th>B/A</th>
</tr>
</thead>
<tbody>
<tr>
<td>Dry (O_2)</td>
<td>(7.72 \times 10^7) (\mu\text{m}^2) (\text{hr}^{-1})</td>
<td>(2.0 \times 10^7) (\mu\text{m} \times \text{hr}^{-1})</td>
<td>(6.23 \times 10^6) (\mu\text{m} \times \text{hr}^{-1})</td>
<td>(2.0 \times 10^6) (\mu\text{m} \times \text{hr}^{-1})</td>
</tr>
<tr>
<td>Wet (O_2)</td>
<td>(2.14 \times 10^7) (\mu\text{m}^2) (\text{hr}^{-1})</td>
<td>(1.23) (\text{eV})</td>
<td>(2.05) (\text{eV})</td>
<td></td>
</tr>
<tr>
<td>(H_2O)</td>
<td>(3.86 \times 10^2) (\mu\text{m}^2) (\text{hr}^{-1})</td>
<td>(0.78) (\text{eV})</td>
<td>(2.05) (\text{eV})</td>
<td></td>
</tr>
</tbody>
</table>

* Above theory is great ... but usually, the equations are not used in practice, since measured data is available

쇄 Rather, oxidation growth charts are used
Using the Oxidation Growth Charts

Example:
* <100> silicon
* Starting oxide thickness: $X_i = 100\text{nm}$
* Want to do wet oxidation at $1000^\circ\text{C}$ to achieve $X_{ox} = 230\text{nm}$
* What is the time $t$ required for this?

Growth Chart for <100> Silicon
Factors Affecting Oxidation

• In summary, oxide thickness is dependent upon:
  1. Time of oxidation
  2. Temperature of oxidation
  3. Partial pressure of oxidizing species ($\propto N_0$)

• Also dependent on:
  4. Reactant type:
     - Dry $O_2$
       - Water vapor $\Rightarrow$ faster oxidation, since water has a higher solubility (i.e., $D$) in $SiO_2$ than $O_2$
  5. Crystal orientation:
     - $<111>$ $\leftarrow$ faster, because there are more bonds available at the Si-surface
     - $<100>$ $\leftarrow$ fewer interface traps; smaller # of unsatisfied Si-bonds at the Si-$SiO_2$ interface

6. Impurity doping:
   - P: increases linear rate const.
     - no affect on parabolic rate constant
     - faster initial growth $\Rightarrow$ surface reaction rate limited
   - B: no effect on linear rate const.
     - increases parabolic rate const.
     - faster growth over an initial oxide $\Rightarrow$ diffusion faster
Thin Film Deposition

• Methods for film deposition:
  - Evaporation
  - Sputter deposition
  - Chemical vapor deposition (CVD)
  - Plasma enhanced chemical vapor deposition (PECVD)
  - Epitaxy
  - Electroplating
  - Atomic layer deposition (ALD)

Evaporation:
• Heat a metal (Al, Au) to the point of vaporization
• Evaporate to form a thin film covering the surface of the Si wafer
• Done under vacuum for better control of film composition
Evaporation

Filament Evaporation System:

1. Pump down to vacuum \( \rightarrow \) reduces film contamination and allows better thickness control
2. Heat W filament \( \rightarrow \) melt Al, wet filament
3. Raise temperature \( \rightarrow \) evaporate Al

\[
\lambda = \frac{kT}{\sqrt{2\pi Pd^2}}
\]

- \( k \) = Boltzmann Constant
- \( T \) = temperature
- \( P \) = pressure
- \( d \) = diameter of gas molecule

Evaporation (cont.)

- \( \lambda \) can be \( \approx 60 \text{m} \) for a 4Å particle at \( 10^{-4} \text{ Pa} \) (0.75 \( \mu \text{Torr} \))
- thus, at 0.75 \( \mu \text{Torr} \), get straight line path from Al staple filament to wafer

Problem: Shadowing & Step Coverage

Get an open source

Solns:
1. Rotate water during evaporation
2. Etch more gradual sidewalls

Better Solution: forget evaporation \( \rightarrow \) sputter deposit the film!
Sputter Deposition

* Use an energetic plasma to dislodge atoms from a material target, allowing the atoms to settle on the wafer surface

```
Target (Al, SiO₂, Si₃N₄, ZnO, Ti, ...)
Ar⁺ plasma

Vacuum Pump

wafer
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Not as low a vacuum as evaporation (~100 Pa) (750 mTorr)

Sputter Deposition Process

* Step-by-step procedure:

1. Pump down to vacuum
   
   \[(~100 \text{ Pa}) \rightarrow 1 \text{ Pa} = 9.8 \times 10^{-6} \text{ atm} \left(\frac{760 \text{ Torr}}{\text{atm}}\right) = 0.0075012 \text{ Torr}\]

   7.5 mTorr

2. Flow gas (e.g., Ar)

3. Fire up plasma (create Ar⁺ ions) → apply dc-bias (or RF for non-conductive targets)

4. Ar⁺ ions bombard target (dislodge atoms)

5. Atoms make their way to the wafer in a more random fashion, since at this higher pressure, \( \lambda \approx 60 \mu \text{m} \) for a 4Å particle; plus, the target is much bigger

* Result: better step coverage!
**Problems With Sputtering**

1. Get some Ar in the film
2. Substrate can heat up
   - up to ~350°C, causing nonuniformity across the wafer
   - but it still is more uniform than evaporation!
3. Stress can be controlled by changing parameters (e.g., flow rate, plasma power) from pass to pass, but repeatability is an issue

*Solution: use Chemical Vapor Deposition (CVD)*

**Chemical Vapor Deposition (CVD)**

* Even better conformity than sputtering
* Form thin films on the surface of the substrate by thermal decomposition and/or reaction of gaseous compounds
  - Desired material is deposited directly from the gas phase onto the surface of the substrate
  - Can be performed at pressures for which \( \lambda \) (i.e., the mean free path) for gas molecules is small
  - This, combined with relatively high temperature leads to

**Excellent Conformal Step Coverage!**

*Types of films: polysilicon, SiO\(_2\), silicon nitride, SiGe, Tungsten (W), Molybdenum (M), Tantalum (Ta), Titanium (Ti), ...*
The CVD Process

**Step-by-Step CVD Sequence:**

1. Reactant gases (+ inert diluting gases) are introduced into the reaction chamber
2. Gas species move to the substrate
3. Reactants adsorb onto the substrate
4. Atoms migrate and react chemically to form films
   - This determines the ultimate conformality of the film (i.e., determines step coverage)
5. Reaction by-products desorbed and removed from reaction chamber

**Surface processes**
- Not Conformal
  - low T
  - not enough adatom migration
- Conformal
  - High T
  - Plenty of adatom migration

**Gas phase processes**

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CVD Modeling

Simplified Schematic:

\[ N_g = \text{conc. of reactant molecules in the gas stream} \]
\[ N_s = \text{conc. of reactant molecules at the surface} \]
\[ J_s = \text{flux of gas molecules at the surface} \]
\[ J_g = \text{flux of molecules diffusing in from the gas stream} \]

**Governing Equations:**

- **Effective diffusion const. for the gas molecule**
  \[ J_s = k_s N_s \quad [k_s = \text{surface reaction rate const.}] \]
  \[ J_g = \left( \frac{D_g}{\delta} \right)(N_g - N_s) = h_g(N_g - N_s) \]

- **Vapor phase mass-transfer coefficient**

CVD Modeling (cont.)

\[ [J_s = J_g = J], \quad N_s = \frac{J_s}{k_s} \]

Otherwise reactants will build up somewhere!

\[ J\left(1 + \frac{h_g}{k_s}\right) = h_g N_g \rightarrow J = \frac{k_s h_g}{k_s + h_g} N_g = (k_s || h_g) N_g \]

**growth rate = \frac{\text{flux}}{\text{# molecules incorporated/unit volume}} = \frac{J}{N} \]

\[ = \frac{J}{N} = \frac{k_s h_g}{k_s + h_g} N_g = \left( k_s \parallel h_g \right) \frac{N_g}{N} = \text{growth rate} \]
CVD Modeling (cont.)

• Case: \( k_s \gg h_g \)
  \( \implies \) surface reaction rate >> mass transfer rate
  \[
  \text{growth rate} = h_g \frac{N_g}{N} \quad (\text{mass-transfer-limited})
  \]

• Case: \( h_g \gg k_s \)
  \( \implies \) mass transfer rate >> surface reaction rate
  \[
  \text{growth rate} = k_s \frac{N_g}{N} \quad (\text{surface-reaction-limited})
  \]
  \[ \sim R_o^{-E_a/kT} \] (Arrhenius character)

Temperature Dependence of CVD

Log (growth rate) vs. temperature graph

- Mass Transport Limited Regime
- Reaction Rate Limited Regime
- Arrhenius behavior

Dep. Rate less dependent on T, here 
\( \implies \) for better control, better to operate here (@ higher T)
Atmospheric Pressure Reactor (APCVD)

* Once used for silicon dioxide passivation in integrated circuits
* Substrates fed continuously
* Large diameter wafers
* Need high gas flow rates
* Mass transport-limited regime (high pressure, so tougher for gas to get to the wafer surface)

* Problems/Issues:
  - Wafers lay flat, and thus, incorporate foreign particles
  - Poor step coverage

Low Pressure Reactor (LPCVD)

* Many films available: polysilicon, SiGe, Si₃N₄, SiO₂, phosphosilicate glass (PSG), BPSG, W

* Temp.: 300 → 1150°C
* Press.: 30 → 250 Pa (200mTorr → 2Torr)
* Reaction rate limited; reduced pressure gives gas molecular high diffusivity; can supply reactants very fast!
* Can handle several hundred wafers at a time
* Excellent uniformity

* Problems:
  - Low dep. rate (compared to atm.)
  - Higher T (than atmospheric)
  - In hot wall reactors, get deposition on tube walls (must clean)
Plasma-Enhanced CVD Reactor (PECVD)

- RF-induced glow discharge + thermal energy to drive reactions → allows lower temperature deposition with decent conformability
- Still low pressure

Problems:
- Pin-holes
- Non-stoichiometric films
- Incorporation of H\textsubscript{2}, N\textsubscript{2}, O\textsubscript{2} contaminants in film; can lead to outgassing or bubbling in later steps

Polysilicon CVD

Polysilicon Deposition:

- Fairly high temperature → conformal
  - 600°C
  - SiH\textsubscript{4} → Si + 2H\textsubscript{2} (thermal decomposition of silane) (conformal → high T)

- LPCVD (25 to 150 Pa) → 100-200Å/min

- In situ doping of polysilicon:
  - n-type: add PH\textsubscript{3} (phosphine) or Arsine gases (but greatly reduces dep. rate)
  - p-type: add diborane gas (greatly increases dep. Rate)
**Silicon Oxide CVD**

**Silicon Dioxide Deposition:**
- After metallization (e.g., over aluminum)
  - Temperature cannot exceed the Si–Al eutectic pt.: 577°C
  - Actually, need lower than this (<500°C) to prevent hillocks from growing on Al surfaces
  - Similar issues for copper (Cu) metallization
- Low temperature reactions:
  - \( \text{SiH}_4 + O_2 \rightarrow \text{SiO}_2 + 2\text{H}_2 \) (silane) ~300-500°C
  - \( 4\text{PH}_3 + 5\text{O}_2 \rightarrow 2\text{P}_2\text{O}_5 + 6\text{H}_2 \) (phosphine) ~300-500°C

  Phosphosilicate glass (PSG)

- Above reactions: not very conformal step coverage → need higher T for this

**Silicon Oxide CVD (cont.)**

- Phosphosilicate glass can be reflown
  - 6-8 wt. % allows reflow @ 1000-1100°C
  - Very useful to achieve smoother topography
  - Lower concentration → won’t reflow
  - Higher concentration → corrodes Al if moisture is present
  - 5-15% P can be used as a diffusion source to dope Si
- Before metallization:
  - Can use higher temperature → better uniformity and step coverage

  \( \text{SiCl}_2\text{H}_2 + 2\text{N}_2\text{O} \rightarrow \text{SiO}_2 + 2\text{N}_2 + 2\text{HCl} \) ~900°C

  (dichlorosilane) (Nitrous oxide) (nice conformal step coverage)

  or ...

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Silicon Oxide CVD (cont.)

\[ \text{Si(OC}_2\text{H}_5)_4 \rightarrow \text{SiO}_2 + \text{by-products} \]

650-750°C

(Tetraethylorthosilicate) (TEOS)

(excellent uniformity & conformal step coverage)

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Silicon Nitride CVD

Silicon Nitride Deposition:

* First, note that thermal growth is possible:
  - Si in NH\(_3\) @ 1000-1100°C
  - But very slow growth rate, thus, impractical

* LPCVD reactions:

- Silane reaction:
  \[ 3\text{SiH}_4 + 4\text{NH}_3 \rightarrow \text{Si}_3\text{N}_4 + 12\text{H}_2 \]
  (Atm. Press.)

- Dichlorosilane reaction:
  \[ 3\text{SiCl}_2\text{H}_2 + 4\text{NH}_3 \rightarrow \text{Si}_3\text{N}_4 + 6\text{HCl} + 6\text{H}_2 \]
  (LPCVD)

700-800°C

Increase and T = 835°C → Si rich nitride → low stress

Problem: Clobbers your pumps! Expensive to maintain!
Silicon Nitride CVD (cont.)

- Comments on LPCVD nitride films:
  - Hydrogen rich: ~8% H₂
  - High internal tensile stresses: films >1000 Å crack and peel due to excessive stress
  - Can get 2 μm films with Si-rich nitride
  - LPCVD gives high resistivity (10¹⁶ Ω-cm) and dielectric strength (10 MV/cm)

PECVD Nitride:

Nitrogen discharge

\[ \text{SiH}_4 + \text{N}_2 \rightarrow 2\text{SiNH} + 3\text{H}_2 \]

or

\[ \text{SiH}_4 + \text{NH}_3 \rightarrow \text{SiNH} + 3\text{H}_3 \]

PECVD films:

- Non-stoichiometric nitride
- 20-25% H₂ content
- Can control stress
- (10⁴ Ω-cm) resistivity

Metal CVD

CVD Metal Deposition:

Tungsten (W) – deposited by thermal, plasma or optically-assisted decomposition

\[ \text{WF}_6 \rightarrow \text{W} + 3\text{F}_2 \]

or via reaction with H₂:

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

Other Metals – Molybdenum (Mo), Tantalum (Ta), and Titanium (Ti)

\[ 2\text{MCl}_5 + 5\text{H}_2 \rightarrow 2\text{M} + 10\text{HCl}, \]

where M = Mo, Ta, or Ti

(Even Al can be CVD’ed with tri-isobutyl Al ... but other methods are better.)

(Cu is normally electroplated)
Epitaxy

- Use CVD to deposit Si on the surface of a Si wafer
  - Si wafer acts as a seed crystal
  - Can grow a single-crystal Si film (as opposed to poly-Si)

Modeling - similar to CVD → in fact, the model discussed so far for CVD is more relevant to epitaxy than CVD!

\[ \log (\text{growth rate}) \]
\[ \frac{1}{T} \]

- Mass transport limited
- Reaction rate limited

Reactions - can use SiCl\(_4\), SiH\(_4\), SiH\(_2\)Cl\(_2\) for vapor phase epitaxy.

- SiCl\(_4\): Silicon tetrachloride
- SiH\(_4\): silane
- SiH\(_2\)Cl\(_2\): dichlorosilane

Epitaxy (cont.)

Most popular: \[ \text{SiCl}_4 \text{(gas)} + 2\text{H}_2 \text{(gas)} \rightarrow \text{Si} \text{(solid)} + 4\text{HCl} \text{(gas)} \]

\(1200^\circ\text{C}\)

Reverse reaction (i.e., etching) if have excessive HCl → sometimes used before deposition to clean the Si wafer surface.

Also get a competing reaction.

\[ \text{SiCl}_4 \text{(gas)} + \text{Si} \text{(solid)} \leftrightarrow 2\text{SiCl}_2 \text{(gas)} \]

- Too much SiCl\(_4\) → etching rather than growth takes place!
- Growth rate too fast → get polysilicon instead of Si. (> 2\(\mu\)m/min.)

Important that the right conc. of SiCl\(_4\) is used!
Epitaxial Growth Rate Dependencies

Figure 4.2

Epitaxy (cont.)

Alternative reaction: pyrolytic decomposition of silane:

\[ \text{SiH}_4 \xrightarrow{650^\circ C} \text{Si} + 2\text{H}_2 \]

not reversible, low T, no HCl formation

however, requires careful control of the reaction to prevent formation of poly-Si

also, the presence of an oxidizing species causes silica formation

Doping of Epitaxial Layers:

1. Just add impurities during growth: Arsine, diborane, Phosphine

   Control resistivity by varying partial pressure of dopant species

   i. Arsine, Phosphine \(\rightarrow\) slow down the growth rate

   ii. Diborane \(\rightarrow\) enhances growth rate
Doping of Epitaxial Layers

2. Use “autodoping” when growing own heavily-doped substrates
   - Impurity evaporates from wafer (or liberated by Cl etching of surface during dep.)
   - Incorporates into gas stream
   - Impurities dope new layer
   - Examples of autodoping:

   **Bipolar Processing:**
   - $n^+ \text{P-Si}$
   - epitaxy
   - Buried collector to reduce collection R

   **MOS:**
   - $n^+$ epitaxy
   - Dopant gradient helps to prevent latch up and punch through

Atomic Layer Deposition (ALD)
Atomic Layer Deposition (ALD)

- **Fundamental Components:**
  - Self-limiting surface reactions of suitable precursor compounds A & B
  - A & B then form the desired product S in a binary reaction cycle consisting of two sequential half-reactions

- **Remarks:**
  - Both half-reactions must be complete and self-limiting at the monolayer level
  - The total film thickness \( d(\text{tot}) \) can be "digitally" controlled by the number of applied deposition cycles \( N(A/B) \):
    \[
    d(\text{tot}) = d(\text{mono}) \cdot N(A/B)
    \]
  - The reagents A & B in the half reactions are normally chemical reactions
    - But they don't need to be
    - They can also represent a physical process, e.g., heating, irradiation, electrochemical conversion
Advantages of ALD

- Surface limited reaction
  - excellent step coverage and refilling
- Self-limiting mechanism
  - Monolayer deposition
  - Composition control
  - Thickness control (∝ # of cycles)
  - Less sensitive to flow rate & temperature

Note, though, that there's still a temperature growth window:

\[ \text{Condensation} \quad \text{Decomposition} \]
\[ \text{ALD Window} \quad \text{Re-evaporation} \]
\[ \text{monolayer} \quad \text{Incomplete Reaction} \]

200°C to 400°C needed

Must purge completely before the next pulse

Usually mixed with an inert gas to achieve lower effective vapor pressures → slows reaction, but needed to allow rapid pulsing & purging.
* In air H$_2$O vapor is adsorbed on most surfaces, forming a hydroxyl group
* With silicon this forms :Si-O-H (s)
* Place the substrate in the reactor
* Pulse TrimethylAluminum (TMA) into the reaction chamber

\[
\text{Al}(\text{CH}_3)_3 (g) + :\text{Si-O-H} (s) \rightarrow :\text{Si-O-Al}(\text{CH}_3)_2 (s) + \text{CH}_4
\]
TrimethylAluminum (TMA) reacts with the adsorbed hydroxyl groups, until the surface is passivated.

- TMA does not react with itself, so terminates the reaction to one layer.
- This leads to the perfect uniformity of ALD.
- The excess TMA and methane reaction product is pumped away.

After the TMA and methane reaction product is pumped away, water vapor ($H_2O$) is pulsed into the reaction chamber.
H₂O 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:

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

The reaction product methane is pumped away.

Excess H₂O vapor does not react with the hydroxyl surface groups.

Again, get perfect passivation to one atomic layer.
* One TMA and one H$_2$O vapor pulse form one cycle
* Here, three cycles are shown, with approximately 1 Å per cycle
* Each cycle including pulsing and pumping takes, e.g., 3 sec

\[
\begin{align*}
\text{Al(CH}_3\text{)}_3 (g) + \text{:Si-O-H (s)} & \rightarrow \text{:Si-O-Al(CH}_3\text{)}_2 (s) + \text{CH}_4 \\
2 \text{H}_2\text{O (g)} + \text{:Si-O-Al(CH}_3\text{)}_2 (s) & \rightarrow \text{:Si-O-Al(OH)}_2 (s) + 2 \text{CH}_4
\end{align*}
\]

ALD Capability

Excellent conformity, even at the bottom of the trench! (aspect ratio ~60:1)
ALD Versus CVD

<table>
<thead>
<tr>
<th></th>
<th>ALD</th>
<th>CVD</th>
</tr>
</thead>
<tbody>
<tr>
<td>Highly reactive precursors</td>
<td>Less reactive precursors</td>
<td></td>
</tr>
<tr>
<td>Precursors react separately on the substrate</td>
<td>Precursors react at the same time on the substrate</td>
<td></td>
</tr>
<tr>
<td>Precursors must not decompose at process temperature</td>
<td>Precursors can decompose at process temperature</td>
<td></td>
</tr>
<tr>
<td>Uniformity ensured by the saturation mechanism</td>
<td>Uniformity requires uniform flux of reactant and temperature</td>
<td></td>
</tr>
<tr>
<td>Thickness control by counting the number of reaction cycles</td>
<td>Thickness control by precise process control and monitoring</td>
<td></td>
</tr>
<tr>
<td>Surplus precursor dosing acceptable</td>
<td>Precursor dosing important</td>
<td></td>
</tr>
</tbody>
</table>

ALD Versus Other Deposition Methods

<table>
<thead>
<tr>
<th>Method</th>
<th>ALD</th>
<th>MBE</th>
<th>CVD</th>
<th>Sputter</th>
<th>Evapor</th>
<th>PLD</th>
</tr>
</thead>
<tbody>
<tr>
<td>Thickness Uniformity</td>
<td>Good</td>
<td>Fair</td>
<td>Good</td>
<td>Good</td>
<td>Fair</td>
<td>Fair</td>
</tr>
<tr>
<td>Film Density</td>
<td>Good</td>
<td>Good</td>
<td>Good</td>
<td>Good</td>
<td>Poor</td>
<td>Good</td>
</tr>
<tr>
<td>Step Coverage</td>
<td>Good</td>
<td>Poor</td>
<td>Varies</td>
<td>Poor</td>
<td>Poor</td>
<td>Poor</td>
</tr>
<tr>
<td>Interface Quality</td>
<td>Good</td>
<td>Good</td>
<td>Varies</td>
<td>Poor</td>
<td>Good</td>
<td>Varies</td>
</tr>
<tr>
<td>Number of Materials</td>
<td>Fair</td>
<td>Good</td>
<td>Poor</td>
<td>Good</td>
<td>Fair</td>
<td>Poor</td>
</tr>
<tr>
<td>Low Temp. Deposition</td>
<td>Good</td>
<td>Good</td>
<td>Varies</td>
<td>Good</td>
<td>Good</td>
<td>Good</td>
</tr>
<tr>
<td>Deposition Rate</td>
<td>Fair</td>
<td>Poor</td>
<td>Good</td>
<td>Good</td>
<td>Good</td>
<td>Good</td>
</tr>
<tr>
<td>Industrial Apps.</td>
<td>Good</td>
<td>Fair</td>
<td>Good</td>
<td>Good</td>
<td>Good</td>
<td>Poor</td>
</tr>
</tbody>
</table>
Metal Electroplating

- Electroplating: the process using electrical current to coat an electrically conductive object with a thin layer of metal
- Useful when very thick (>1 μm) metal films are needed
- Evaporation and sputtering generally suffer from excessive stress when films get too thick → get peeling

1. Switch on external supply of direct current
2. Metal at anode is oxidized to form cations with a (+) charge
3. Cations are attracted to the (-) charge on the cathode
4. Cations get reduced by e⁻'s at the cathode, depositing the metal (in this case, Cu)
**Wafer-Level Implementation**

- **Wafer Preparation:** areas where plating is to occur must have electrical access to the DC voltage source.
  - Often use a seed layer that accesses all plating locations.

  - **Al layer insures electrical contact to plating areas, despite patterned Ti/Au**
  - Need not be the metal to be electroplated.
    - Often just a platinum electrode.
    - In this case, must replenish electrolytic solution after time.