


EE C247B - ME C218 Introduction to MEMS Design Spring 2018

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Lecture Module 3: Oxidation & Film Deposition

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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

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MEMS Fabrication

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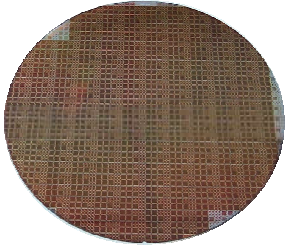
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Making Mechanical Devices

- 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



Automobile Assembly Line



CMOS Integrated Circuit Wafer

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Polysilicon Surface-Micromachining

Labels in diagram: Nitride, Isolation Oxide, Interconnect Polysilicon, Sacrificial Oxide, Structural Polysilicon, Silicon Substrate, Hydrofluoric Acid Release Etchant, Wafer, Free-Standing Polysilicon Beam, Silicon Substrate.

- Uses IC fabrication instrumentation exclusively
- Variations: sacrificial layer thickness, fine- vs. large-grained polysilicon, *in situ* vs. POCL₃-doping

**300 kHz Folded-Beam
 Micromechanical Resonator**

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Electroplating: Metal MEMS

Labels in diagram: Photoresist, Aluminum, Silicon Substrate, Wafer, Aluminum Release Etchant, Suspended Nickel Microstructure, Electrode, Nickel, Ti/Au, Si₃N₄ Isolation, Silicon Substrate.

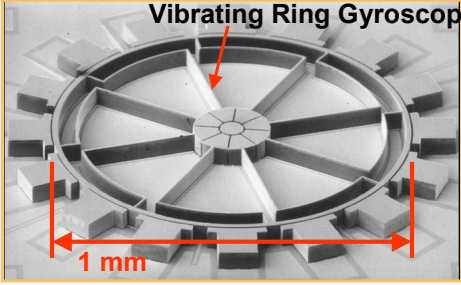
- Use electroplating to obtain metal μ structures
- When thick: call it "LIGA"
- Pros: fast low temp deposition, very conductive
- Cons: drift, low mech. Q
 ↪ but may be solvable?

RF Switch

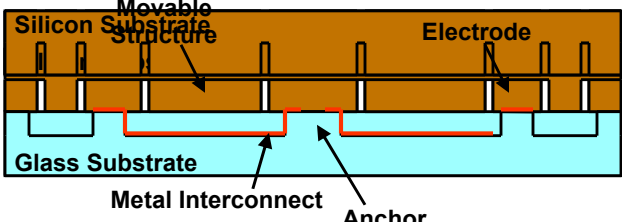
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Bulk Micromachining and Bonding


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



Micromechanical Vibrating Ring Gyroscope
[Najafi, Michigan]



Movable Structure
Silicon Substrate
Electrode
Glass Substrate
Metal Interconnect
Anchor



[Pisano, UC Berkely]
Microrotor (for a microengine)

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Oxidation

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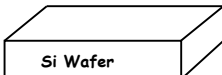
Thermal Oxidation of Silicon

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- 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:

<u>For dry oxygen:</u>	<u>For water vapor:</u>
$\text{Si} + \text{O}_2 \rightarrow \text{SiO}_2$	$\text{Si} + 2\text{H}_2\text{O} \rightarrow \text{SiO}_2 + 2\text{H}_2$

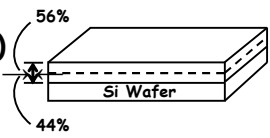
Schematically:



Si Wafer

High T (~900°C - 1200°C)

In dry O₂
or
Water vapor




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Oxidation Modeling

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(1) Initially: (no oxide @ surface)

gas stream




Si

↪ Growth rate determined by reaction rate @ the surface

(2) As oxide builds up:

gas stream



oxide

Si

↪ Reactant must diffuse to Si surface where the oxidation reaction takes place

↪ Growth rate governed more by rate of diffusion to the silicon-oxide interface

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Oxidation Modeling (cont.)

N_o = reactant conc. at oxide surface [in cm^{-2}]
 N_i = reactant conc. at Si-SiO₂ interface
 J = reactant flux = $-D \frac{\partial N(x,t)}{\partial x}$ [Fick's 1st Law of Diffusion]
 Diffusion coeff. [in $\mu\text{m/hr}$ or m/s]
 distance from surface

In the SiO₂:

$$J = D \frac{(N_o - N_i)}{X_{ox}} = \text{constant} \quad (1)$$

[in # particles/(cm²·s)] Assumption that the reactant does not accumulate in the oxide.

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Oxidation Modeling (cont.)

At the Si-SiO₂ interface:
 Oxidation rate $\propto N_i \therefore J \propto N_i \Rightarrow J = k_s N_i \quad (2)$

Reaction rate constant @ Si-SiO₂ interface

Combining (1) and (2):

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

$$JX_{ox} = DN_o - \frac{DJ}{k_s} \rightarrow J \left(X_{ox} + \frac{D}{k_s} \right) = DN_o$$

$$\therefore J = \frac{DN_o}{X_{ox} + \frac{D}{k_s}} = \text{Flux of reactants}$$

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Oxidation Modeling (cont.)

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

oxidizing flux

Rate of change of oxide layer thickness w/time }
$$= \frac{dX_{OX}}{dt} = \frac{J}{M} = \frac{DN_O/M}{X_{OX} + D/k_s} \quad (3)$$

of molecules of oxidizing species incorporated into a unit volume of oxide }
$$\begin{cases} = 2.2 \times 10^{22} \text{ cm}^{-3} \text{ for } O_2 \\ = 4.4 \times 10^{22} \text{ cm}^{-3} \text{ for } H_2O \end{cases}$$

Solve (3) for $X_{OX}(t)$: [Initial condition $X_{OX}(t=0) = X_i$]

$$\frac{dX_{OX}}{dt} = \frac{DN_O/M}{X_{OX} + D/k_s} \Rightarrow \int_{X_i}^{X_{OX}} \left(X_{OX} + \frac{D}{k_s} \right) dX_{OX} = \int_0^t \frac{DN_O}{M} dt$$

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Oxide Thickness Versus Time

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Result:

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

time required to grow X_i [X_i = initial oxide thickness]

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

where $A = \frac{2D}{k_s}$ $\tau = \frac{X_i^2}{B} + \frac{X_i}{(B/A)}$

$B = \frac{2DN_O}{M}$ $D = D_o \exp\left(-\frac{E_A}{kT}\right)$

[i.e., D governed by an Arrhenius relationship \rightarrow temperature dependent]

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Oxidation Modeling (cont.)

For shorter times:

$$\left[(t + \tau) \ll \frac{A^2}{4B} \right] \Rightarrow X_{OX}(t) = \left(\frac{B}{A} \right) (t + \tau) \Rightarrow \text{oxide growth limited by reaction at the Si-SiO}_2 \text{ interface}$$

Taylor expansion (first term after 1's cancel) linear growth rate constant

For long oxidation times: oxide growth diffusion-limited

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

$t \gg \tau$ Parabolic rate constant

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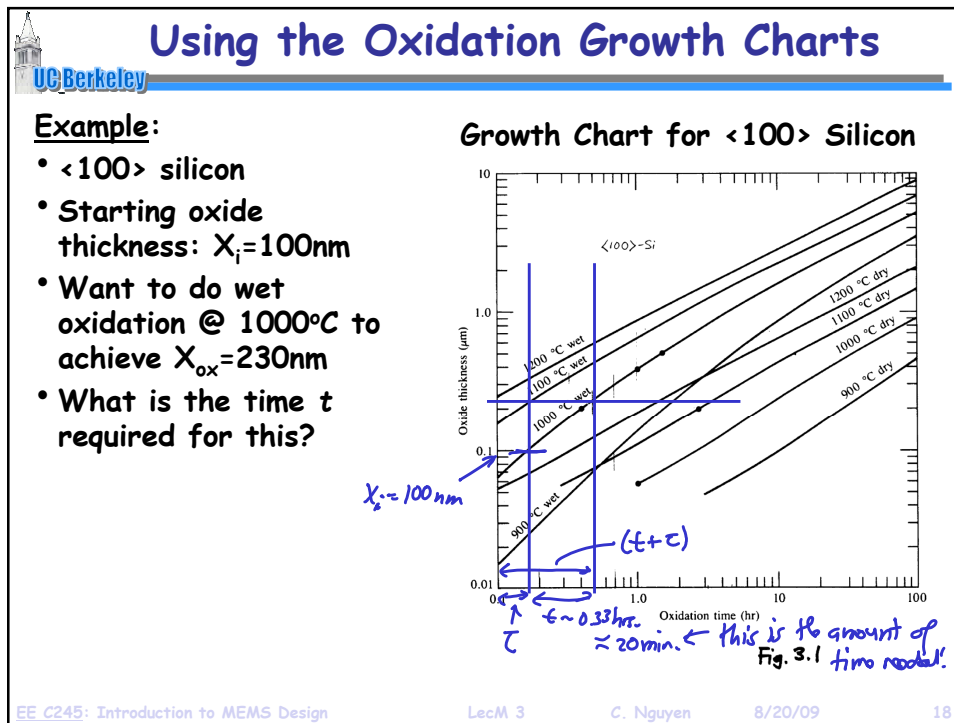
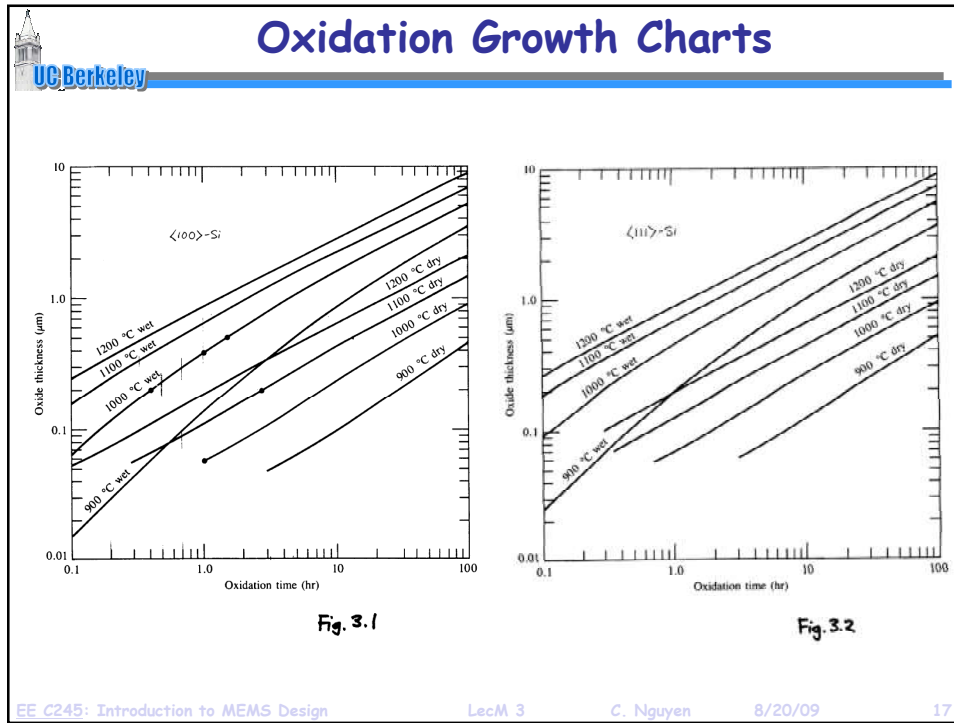
Oxidation Rate Constants


Table 6-2 Rate constants describing (111) silicon oxidation kinetics at 1 Atm total pressure. For the corresponding values for (100) silicon, all C_2 values should be divided by 1.68.

Ambient	B	B/A
Dry O ₂	$C_1 = 7.72 \times 10^2 \mu\text{m}^2 \text{hr}^{-1}$	$C_2 = 6.23 \times 10^6 \mu\text{m hr}^{-1}$
	$E_1 = 1.23 \text{ eV}$	$E_2 = 2.0 \text{ eV}$
Wet O ₂	$C_1 = 2.14 \times 10^2 \mu\text{m}^2 \text{hr}^{-1}$	$C_2 = 8.95 \times 10^7 \mu\text{m hr}^{-1}$
	$E_1 = 0.71 \text{ eV}$	$E_2 = 2.05 \text{ eV}$
H ₂ O	$C_1 = 3.86 \times 10^2 \mu\text{m}^2 \text{hr}^{-1}$	$C_2 = 1.63 \times 10^8 \mu\text{m hr}^{-1}$
	$E_1 = 0.78 \text{ eV}$	$E_2 = 2.05 \text{ eV}$

- Above theory is great ... but usually, the equations are not used in practice, since measured data is available
 - ↳ Rather, oxidation growth charts are used


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 **Factors Affecting Oxidation**

- In summary, oxide thickness is dependent upon:
 1. Time of oxidation
 2. Temperature of oxidation
 3. Partial pressure of oxidizing species ($\propto N_o$)
- 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:
 - $\langle 111 \rangle \leftarrow$ faster, because there are more bonds available at the Si-surface
 - $\langle 100 \rangle \leftarrow$ fewer interface traps; smaller # of unsatisfied Si-bonds at the Si- SiO_2 interface

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 **Factors Affecting Oxidation**


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

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Thin Film Deposition

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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

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Evaporation

Filament Evaporation System:

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

$$\text{mean free path} = \lambda = \frac{kT}{\sqrt{2\pi Pd^2}}$$

Vacuum Pump

k = Boltzmann Constant
T = temperature
P = pressure
d = diameter of gas molecule

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Evaporation (cont.)

- λ can be $\sim 60\text{m}$ for a 4\AA particle at 10^{-4} 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

Problem: line of sight deposition

Solns:

- i. Rotate wafer during evaporation
- ii. Etch more gradual sidewalls

Better Solution: forget evaporation → sputter deposit the film!

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Sputter Deposition

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

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

Vacuum Pump

Target (Al, SiO₂, Si₃N₄, ZnO, Ti, ...)

plasma

Ar⁺

Ar⁺

wafer


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Sputter Deposition Process

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- Step-by-step procedure:**
 - Pump down to vacuum
 $(\sim 100 \text{ Pa}) \rightarrow 1 \text{ Pa} = 9.8 \times 10^{-6} \text{ atm} \left(\frac{760 \text{ Torr}}{\text{atm}} \right) = 0.0075012 \text{ Torr}$
 ← 7.5 mTorr
 - Flow gas (e.g., Ar)
 - Fire up plasma (create Ar⁺ ions) → apply dc-bias (or RF for non-conductive targets)
 - Ar⁺ ions bombard target (dislodge atoms)
 - Atoms make their way to the wafer in a more random fashion, since at this higher pressure, $\lambda \sim 60 \mu\text{m}$ for a 4 Å particle; plus, the target is much bigger
- Result:** better step coverage!


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 **Problems With Sputtering**

1. Get some Ar in the film
2. Substrate can heat up
 - ↪ up to $\sim 350^{\circ}\text{C}$, 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)

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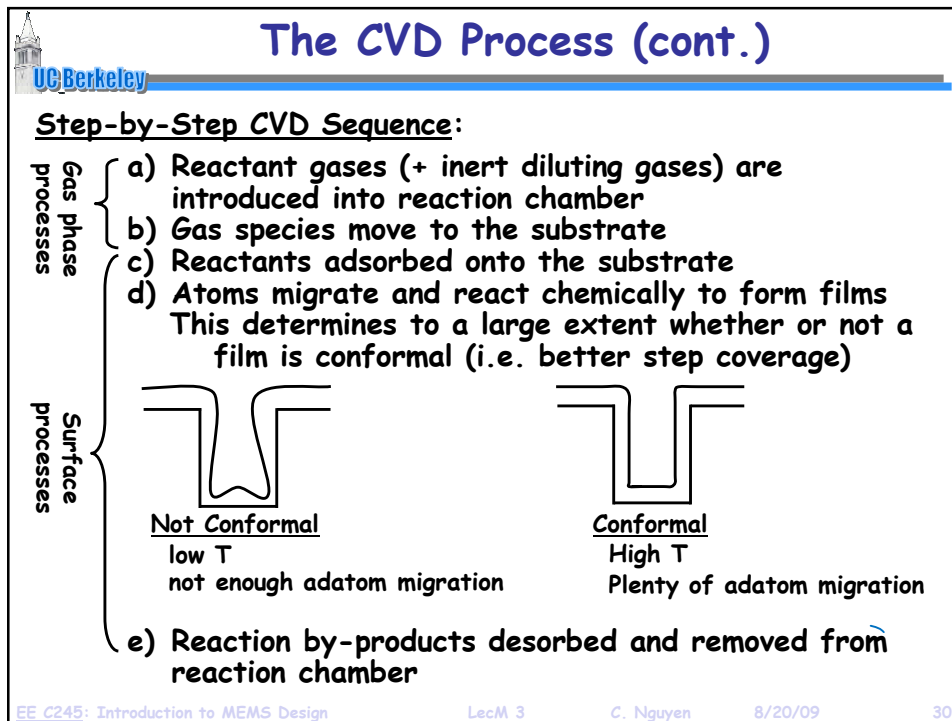
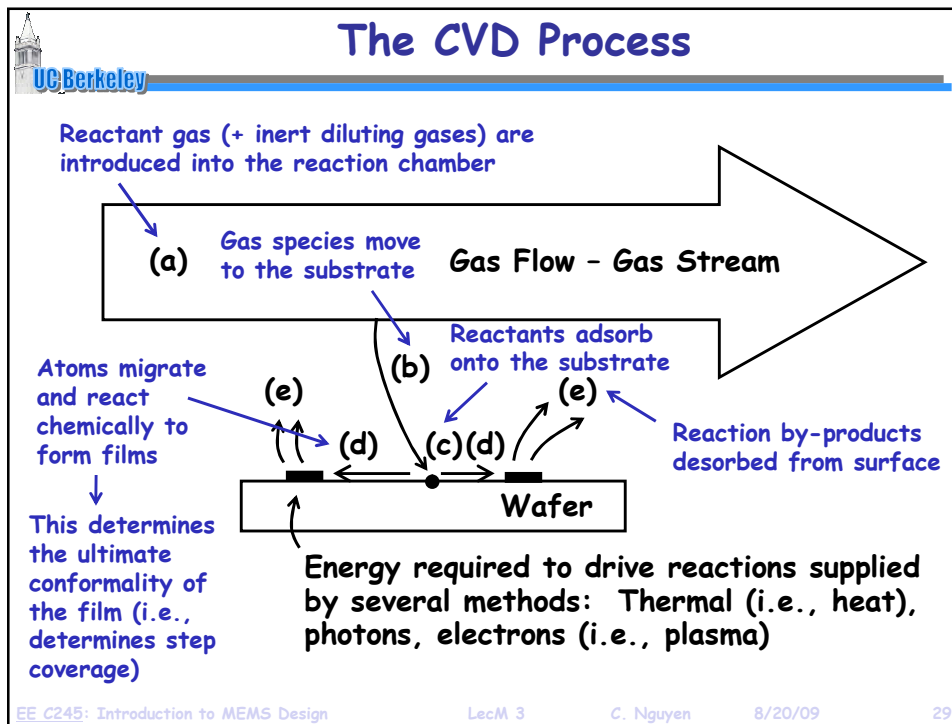
 **Chemical Vapor Deposition (CVD)**

- 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 λ (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), ...

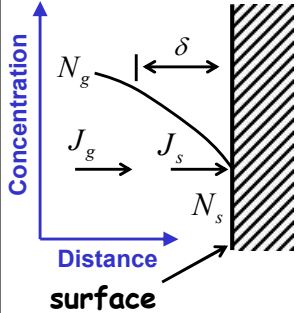
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CVD Modeling



Simplified Schematic:



N_g = conc. of reactant molecules in the gas stream
 N_s = conc. of reactant molecules at the surface
 J_s = flux of gas molecules at the surface
 J_g = flux of molecules diffusing in from the gas stream

Governing Equations:

Effective diffusion const. for the gas molecule


$$J_s = k_s N_s \quad [k_s = \text{surface reaction rate const.}]$$

Vapor phase mass-transfer coefficient

$$J_g = \left(\frac{\bar{D}_g}{\delta} \right) (N_g - N_s) = h_g (N_g - N_s)$$

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CVD Modeling (cont.)



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

Otherwise reactants will build up somewhere!

$$J = h_g \left(N_g - \frac{J}{k_s} \right) = h_g N_g - \frac{h_g J}{k_s}$$

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

flux

molecules incorporated/unit volume

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

$$= \frac{J}{N} = \frac{k_s h_g}{k_s + h_g} \frac{N_g}{N} = (k_s || h_g) \frac{N_g}{N} = \text{growth rate}$$

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CVD Modeling (cont.)

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- **Case:** $k_s \gg h_g$
 ↳ surface reaction rate \gg mass transfer rate

$$\text{growth rate} = h_g \frac{N_g}{N}$$

(mass-transfer-limited)

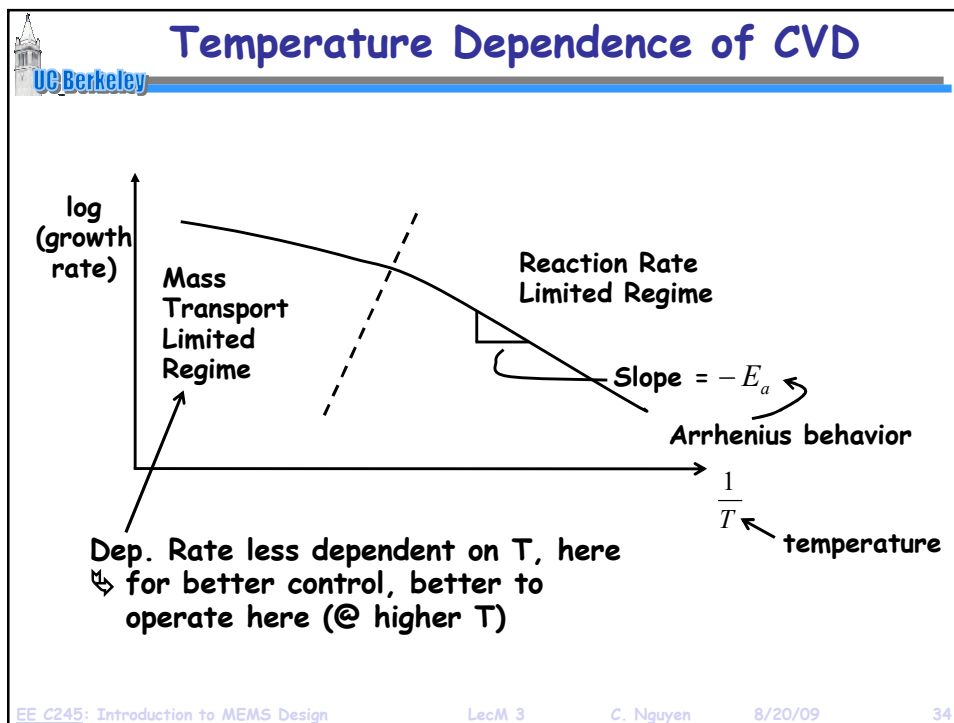
- **Case:** $h_g \gg k_s$
 ↳ mass transfer rate \gg surface reaction rate

$$\text{growth rate} = k_s \frac{N_g}{N}$$

(surface-reaction-limited)

$\sim R_o^{-E_a/kT}$ (Arrhenius character)

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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

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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)

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Plasma-Enhanced CVD Reactor (PECVD)

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- 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 H₂, N₂, O₂ contaminants in film; can lead to outgassing or bubbling in later steps

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Polysilicon CVD

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Polysilicon Deposition:

$$\text{SiH}_4 \xrightarrow{600^\circ\text{C}} \text{Si} + 2\text{H}_2 \quad (\text{thermal decomposition of silane})$$
 Fairly high temperature → conformal
 (conformal → high T)

LPCVD (25 to 150 Pa) → 100-200Å/min

- **In situ doping of polysilicon:**
 - ↪ n-type: add PH₃ (phosphine) or Arsine gases (but greatly reduces dep. rate)
 - ↪ p-type: add diborane gas (greatly increases dep. Rate)

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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:

LPCVD LTO Reactions	}	$\text{SiH}_4 + \text{O}_2 \xrightarrow[300-500^\circ\text{C}]{\text{(silane)}} \text{SiO}_2 + 2\text{H}_2$
		$4\text{PH}_3 + 5\text{O}_2 \xrightarrow[300-500^\circ\text{C}]{\text{(phosphine)}} 2\text{P}_2\text{O}_5 + 6\text{H}_2$

↖ Phosphosilicate glass (PSG)

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

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Silicon Oxide CVD (cont.)

- Phosphosilicate glass can be reflow
 - ↳ 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

HTO	}	$\text{SiCl}_2\text{H}_2 + 2\text{N}_2\text{O} \xrightarrow[\sim 900^\circ\text{C}]{} \text{SiO}_2 + 2\text{N}_2 + 2\text{HCl}$
		(dichlorosilane) (Nitrous oxide) (nice conformal step coverage)

or ...

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Silicon Oxide CVD (cont.)

$$\text{Si(OC}_2\text{H}_5)_4 \xrightarrow{650-750^\circ\text{C}} \text{SiO}_2 + \text{by-products}$$

(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 NH₃ @ 1000-1100°C
 - ↪ But very slow growth rate, thus, impractical
- LPCVD reactions:

700-900°C

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


Dichlorosilane reaction:

$$3\text{SiCl}_2\text{H}_2 + 4\text{NH}_3 \xrightarrow[\text{(LPCVD)}]{700-800^\circ\text{C}} \text{Si}_3\text{N}_4 + 6\text{HCl} + 6\text{H}_2$$

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

Problem: Clobbers your pumps! Expensive to maintain!

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Silicon Nitride CVD (cont.)

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

PECVD Nitride:

$\text{SiH}_4 + \text{N}_2 \xrightarrow{\text{Nitrogen discharge}} 2\text{SiNH} + 3\text{H}_2$ <p style="text-align: center;">or</p> $\text{SiH}_4 + \text{NH}_3 \xrightarrow{\text{Ar plasma}} \text{SiNH} + 3\text{H}_3$	}	<p>PECVD films:</p> <ul style="list-style-type: none"> ↗ Non-stoichiometric nitride ↗ 20-25% H₂ content ↗ Can control stress ↗ (10⁶ Ω-cm) resistivity
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Metal CVD

CVD Metal Deposition:

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

$$\text{WF}_6 \longrightarrow \text{W} + 3\text{F}_2$$

or via reaction with H₂:

$$\text{WF}_6 + 3\text{H}_2 \longrightarrow \text{W} + 6\text{HF}$$

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

$$2\text{MCl}_5 + 5\text{H}_2 \longrightarrow 2\text{M} + 10\text{HCl},$$

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)

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Epitaxy

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!

↙ get similar curve:

Reactions - can use SiCl_4 , SiH_4 , SiH_2Cl_2 for vapor phase epitaxy.

SiCl_4 : Silicon tetrachloride
 SiH_4 : silane
 SiH_2Cl_2 : dichlorosilane

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Epitaxy (cont.)

$$\text{SiCl}_4 (\text{gas}) + 2\text{H}_2 (\text{gas}) \xrightarrow{1200^\circ\text{C}} \text{Si} (\text{solid}) + 4\text{HCl} (\text{gas})$$

(Note that this is reversible!) \rightleftharpoons Reverse reaction (i.e., etching) if have excessive HCl → sometimes used before deposition to clean the Si wafer surface.

Also get a competing reaction.

$\text{SiCl}_4 (\text{gas}) + \text{Si} (\text{solid}) \rightleftharpoons 2\text{SiCl}_2 (\text{gas})$

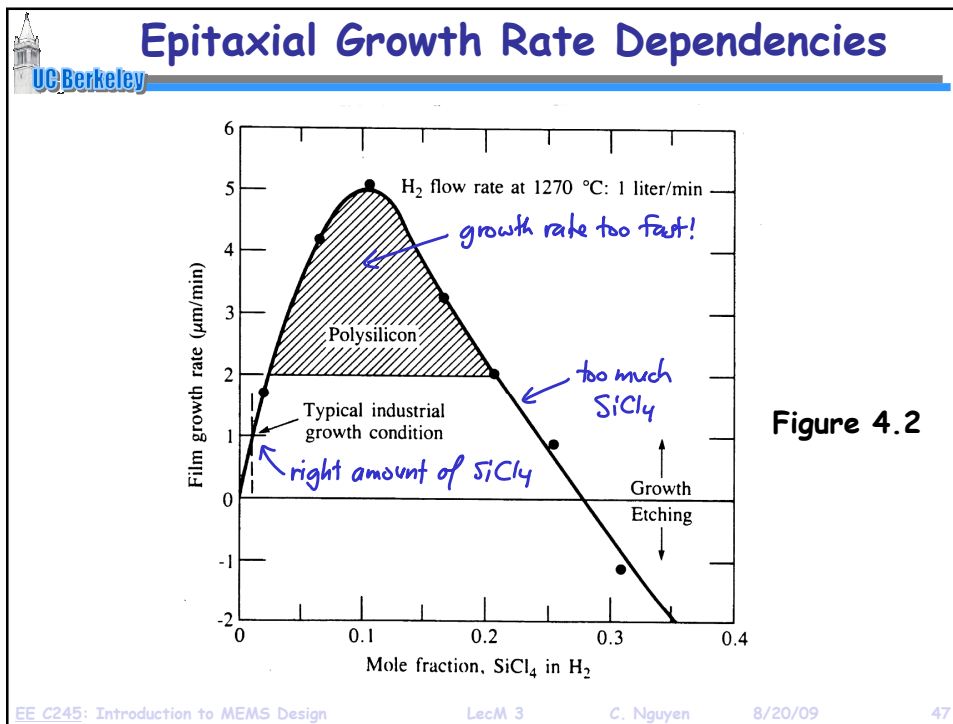
- ↳ Too much SiCl_4 → etching rather than growth takes place!
- ↳ Growth rate too fast → get polysilicon instead of Si. ($> 2\mu\text{m}/\text{min.}$)

}

See
Figure
4.2

Important that the right conc. of SiCl_4 is used!

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Epitaxy (cont.)

Alternative reaction: pyrolytic decomposition of silane:

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


↙ 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 → slow down the growth rate
 - ii. Diborane → enhances growth rate

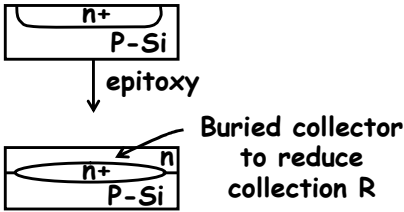
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 **Doping of Epitaxial Layers**

2. Use "autodoping" → when growing own heavily-doped substrates

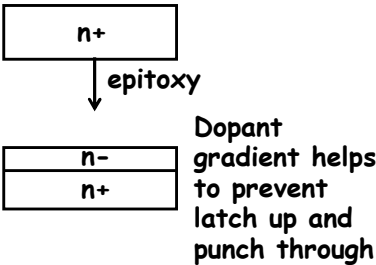
- ↳ Impurity evaporates from wafer (or liberated by Cl etching of surface during dep.)
- ↳ Incorporates into gas stream
- ↳ Impurities dope new layer
- ↳ Examples of autodoping:

Bipolar Processing:




Buried collector to reduce collection R

MOS:



Dopant gradient helps to prevent latch up and punch through

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 **Atomic Layer Deposition (ALD)**

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Atomic Layer Deposition (ALD)

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- **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

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Atomic Layer Deposition (ALD)

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- **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 $N(\text{A/B})$:

$$d(\text{tot}) = d(\text{mono}) \cdot N(\text{A/B})$$

- ↳ 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

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Advantages of ALD

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

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

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ALD Reactor

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200°C to 400°C needed Must purge completely before the next pulse

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Al₂O₃ ALD

The diagram shows a substrate surface (e.g., Si) with several silicon atoms (orange spheres) bonded to hydrogen atoms (blue spheres). One silicon atom is bonded to an oxygen atom (red sphere), which is in turn bonded to a hydrogen atom (blue sphere), forming a hydroxyl group (OH). A molecule of trimethyl aluminum (TMA), Al(CH₃)₃ (purple sphere for Al, red spheres for C, blue spheres for H), is shown above the surface. Labels indicate: 'Tri-methyl aluminum Al(CH₃)_{3(g)}', 'Methyl group (CH₃)', and 'Hydroxyl (OH) from surface adsorbed H₂O'. The substrate surface is labeled 'Substrate surface (e.g. Si)'.

- In air H₂O 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

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Al₂O₃ ALD

The diagram shows the reaction of TMA with the surface hydroxyl group. The TMA molecule is shown reacting with the OH group on the silicon atom. Labels indicate: 'Reaction of TMA with OH' and 'Methane reaction product CH₄'. The silicon atom is now bonded to two methyl groups from the TMA molecule. The substrate surface is labeled 'Substrate surface (e.g. Si)'.

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

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

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Al₂O₃ ALD

The diagram shows a substrate surface (e.g., Si) with a layer of adsorbed hydroxyl groups (OH). A TrimethylAluminum (TMA) molecule (Al(CH₃)₃) is shown reacting with one of these hydroxyl groups. The reaction produces a surface-bound Al-CH₃ group and a methane molecule (CH₄) as a byproduct. Excess TMA and the methane reaction product are shown being pumped away from the surface.

- 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

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Al₂O₃ ALD

The diagram shows the substrate surface after the first step, with a layer of Al-CH₃ groups. A water vapor molecule (H₂O) is shown reacting with one of these Al-CH₃ groups. The reaction produces a surface-bound Al-OH group and a methane molecule (CH₄) as a byproduct.

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

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Al₂O₃ ALD

The diagram shows a surface of aluminum (Al) atoms, represented by purple spheres, with methyl groups (CH₃) attached. A water molecule (H₂O) is shown reacting with one of the methyl groups. The reaction results in a new hydroxyl group (OH) being formed on the Al atom and a methane molecule (CH₄) being released as a reaction product. The Al atom is now bonded to two oxygen atoms (O), which are bridged to the next Al atom on the surface.

- 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

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

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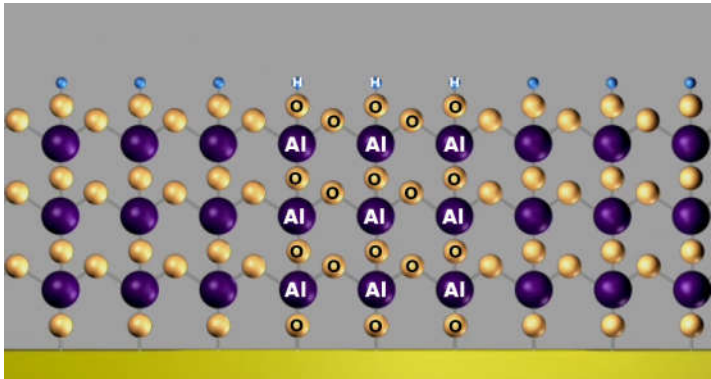
Al₂O₃ ALD

The diagram shows the surface after the reaction. The Al atoms are now fully passivated, forming a continuous layer of Al-O-Al bridges. The surface is now a perfect passivation to one atomic layer.

- 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

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Al₂O₃ ALD



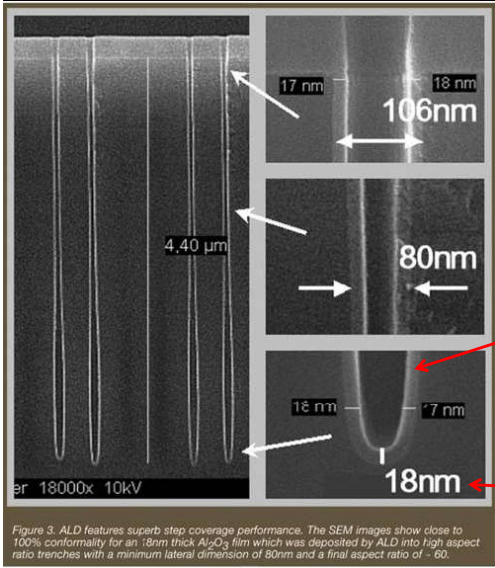
- One TMA and one H₂O vapor pulse form one cycle
- Here, three cycles are shown, with approximately 1 Å per cycle
- Each cycle including pulsing and pumping takes, e.g., 3 sec

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

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

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ALD Capability



Excellent conformality, even at the bottom of the trench! (aspect ratio ~60:1)

Al₂O₃

Figure 3. ALD features superb step coverage performance. The SEM images show close to 100% conformality for an 18nm thick Al₂O₃ film which was deposited by ALD into high aspect ratio trenches with a minimum lateral dimension of 80nm and a final aspect ratio of ~60.

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ALD Versus CVD

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

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ALD Versus Other Deposition Methods

Method	ALD	MBE	CVD	Sputter	Evapor	PLD
Thickness Uniformity	Good	Fair	Good	Good	Fair	Fair
Film Density	Good	Good	Good	Good	Poor	Good
Step Coverage	Good	Poor	Varies	Poor	Poor	Poor
Interface Quality	Good	Good	Varies	Poor	Good	Varies
Number of Materials	Fair	Good	Poor	Good	Fair	Poor
Low Temp. Deposition	Good	Good	Varies	Good	Good	Good
Deposition Rate	Fair	Poor	Good	Good	Good	Good
Industrial Apps.	Good	Fair	Good	Good	Good	Poor

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Electroplating

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Metal Electroplating

- **Electroplating:** the process using electrical current to coat an electrically conductive object with a thin layer of metal
 - ↳ Useful when very thick ($>1\mu\text{m}$) metal films are needed
 - ↳ Evaporation and sputtering generally suffer from excessive stress when films get too thick \rightarrow get peeling

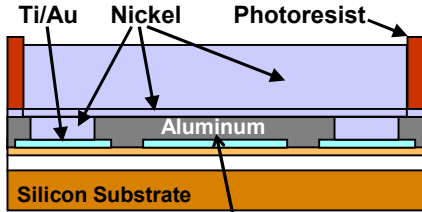
1. Switch on external supply of direct current
2. Metal at anode is oxidized to form cations with a (+) charge
3. Cations are attracted to the (-) charge on the cathode
4. Cations get reduced by e^- 's at the cathode, depositing the metal (in this case, Cu)

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Wafer-Level Implementation

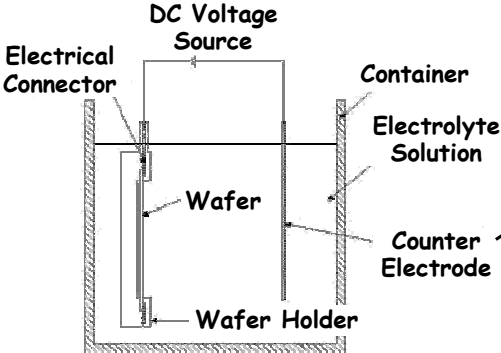
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- **Wafer Preparation:** areas where plating is to occur must have electrical access to the DC voltage source
 - ↳ Often use a seed layer that accesses all plating locations



Ti/Au Nickel Photoresist
Aluminum
Silicon Substrate

Al layer insures electrical contact to plating areas, despite patterned Ti/Au



DC Voltage Source
Electrical Connector
Container
Electrolyte Solution
Counter Electrode
Wafer
Wafer Holder

- Need not be the metal to be electroplated
 - ↳ Often just a platinum electrode
 - ↳ In this case, must replenish electrolytic solution after time

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