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# EE C247B - ME C218 Introduction to MEMS Design Spring 2015

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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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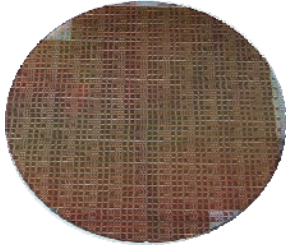
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## Making Mechanical Devices

- 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

- Uses IC fabrication instrumentation exclusively
- Variations: sacrificial layer thickness, fine- vs. large-grained polysilicon, *in situ* vs.  $POCl_3$ -doping

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### Electroplating: Metal MEMS

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

**RF Switch**

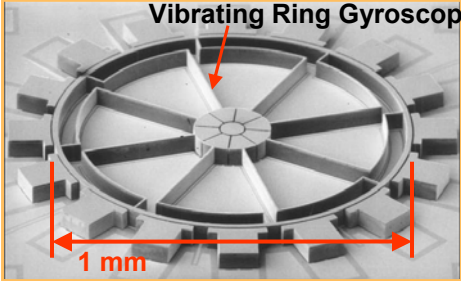
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**Bulk Micromachining and Bonding**

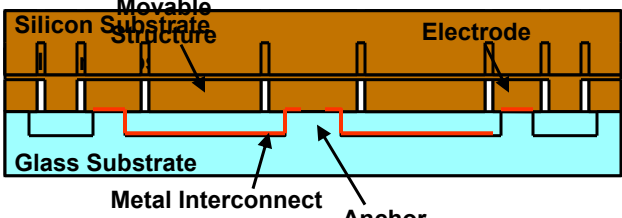
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- Use the wafer itself as the structural material
- *Adv*: very large aspect ratios, thick structures
- *Example*: deep etching and wafer bonding

Micromechanical Vibrating Ring Gyroscope




[Najafi, Michigan]



Movable Structure  
Silicon Substrate  
Electrode  
Glass Substrate  
Metal Interconnect  
Anchor

[Pisano, UC Berkeley]



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:

For dry oxygen:                      For water vapor:  
 $Si + O_2 \rightarrow SiO_2$                $Si + 2H_2O \rightarrow SiO_2 + 2H_2$

Schematically:

High T (~900°C - 1200°C)  
 In dry O<sub>2</sub>  
 or  
 Water vapor

56%  
 44%

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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.)**

$N_0$  = reactant conc. at oxide surface [in  $\text{cm}^{-2}$ ]  
 $N_i$  = reactant conc. at Si-SiO<sub>2</sub> interface  
 $J$  = reactant flux =  $-D \frac{\partial N(x,t)}{\partial x}$  [Fick's 1<sup>st</sup> Law of Diffusion]  
 Diffusion coeff. [in  $\mu\text{m/hr}$  or  $\text{m/s}$ ]  
 distance from surface

**In the SiO<sub>2</sub>:**

$$J = D \frac{(N_0 - N_i)}{X_{ox}} = \text{constant} \quad (1)$$

[in # particles/(cm<sup>2</sup>·s)]      Assumption that the reactant does not accumulate in the oxide.

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**Oxidation Modeling (cont.)**

**At the Si-SiO<sub>2</sub> interface:**  
 Oxidation rate  $\propto N_i \therefore J \propto N_i \Rightarrow J = k_s N_i \quad (2)$

Reaction rate constant @ Si-SiO<sub>2</sub> interface

**Combining (1) and (2):**

$$\left[ N_i = \frac{J}{k_s} \right] \Rightarrow J = D \left( \frac{N_0 - J/k_s}{X_{ox}} \right)$$

$$JX_{ox} = DN_0 - \frac{DJ}{k_s} \rightarrow J \left( X_{ox} + \frac{D}{k_s} \right) = DN_0$$

$$\therefore J = \frac{DN_0}{X_{ox} + \frac{D}{k_s}} = \text{Flux of reactants}$$

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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 }  $= \frac{dX_{OX}}{dt} = \frac{J}{M} = \frac{DN_o/M}{X_{OX} + D/k_s}$  (3)

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

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:**

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

Taylor expansion (first term after 1's cancel)

**For long oxidation times: oxide growth diffusion-limited**

$$\left[ (t + \tau) \gg \frac{A^2}{4B} \right] \Rightarrow X_{OX}(t) = \sqrt{B(t + \tau)} \approx \sqrt{Bt} \quad \begin{matrix} t \gg \tau \\ \text{Parabolic rate constant} \end{matrix}$$

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**Oxidation Rate Constants**

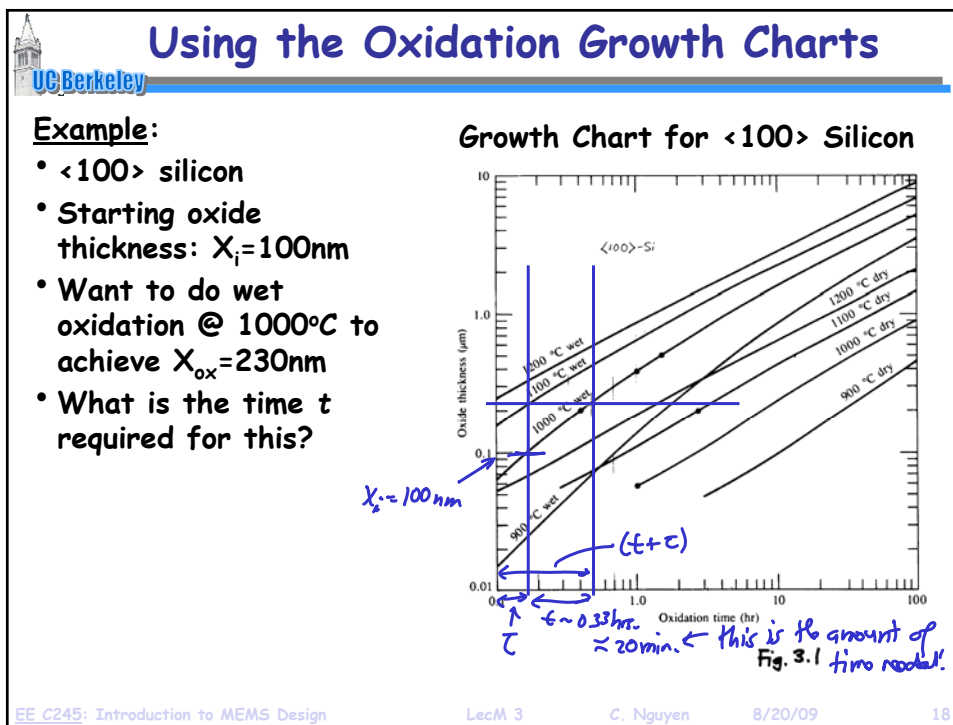
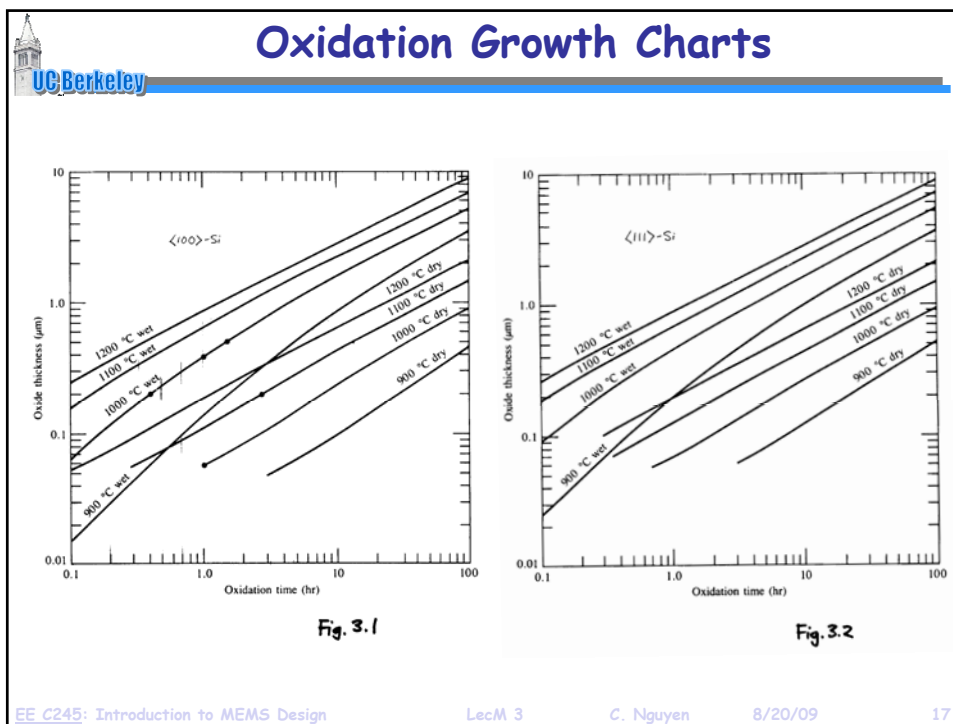
**Table 6-2** Rate constants describing (111) silicon oxidation kinetics at 1 Atm total pressure. For the corresponding values for (100) silicon, all  $C_2$  values should be divided by 1.68.


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

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

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

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### Evaporation (cont.)

•  $\lambda$  can be  $\sim 60\text{m}$  for a  $4\text{\AA}$  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

**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, SiO<sub>2</sub>, Si<sub>3</sub>N<sub>4</sub>, 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<sup>+</sup> ions) → apply dc-bias (or RF for non-conductive targets)
  - Ar<sup>+</sup> 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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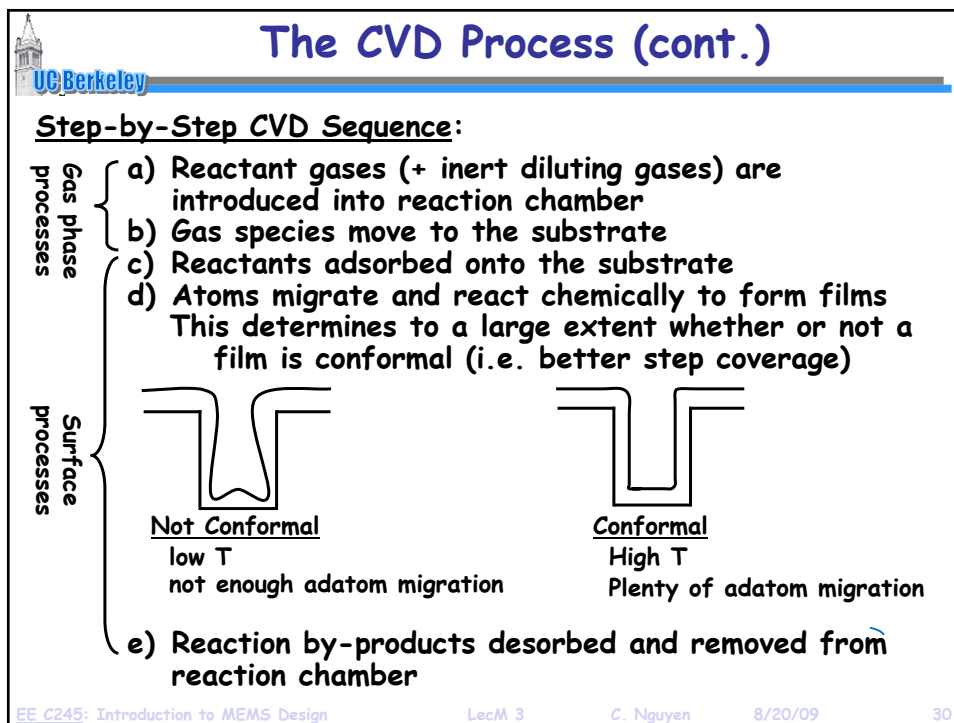
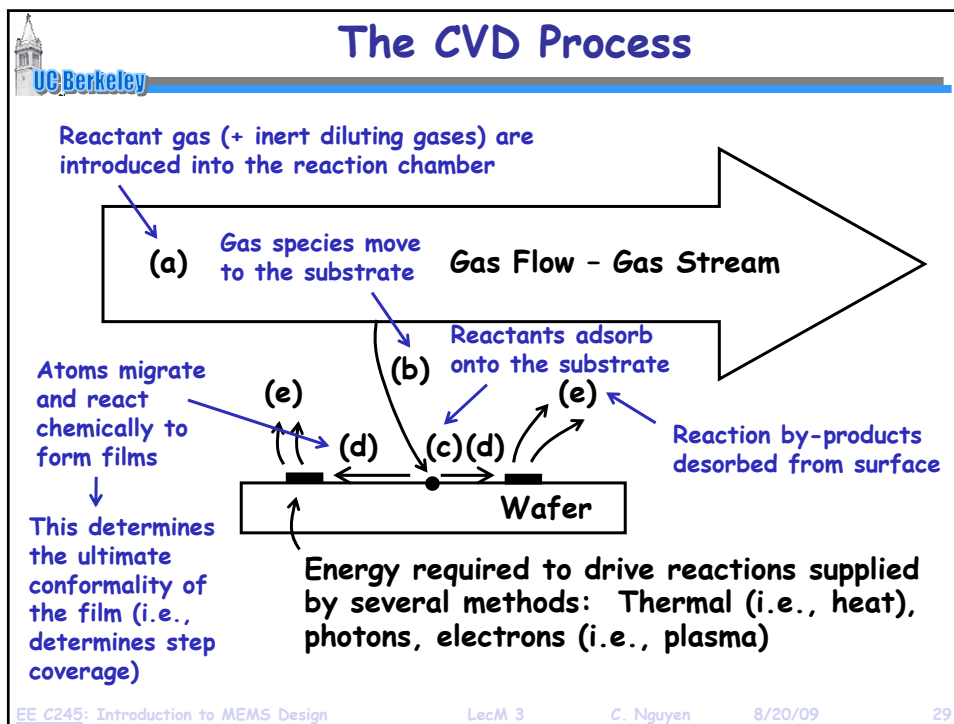
 **Chemical Vapor Deposition (CVD)**


- 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  $\lambda$  (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,  $\text{SiO}_2$ , silicon nitride,  $\text{SiGe}$ , Tungsten (W), Molybdenum (M), Tantalum (Ta), Titanium (Ti), ...

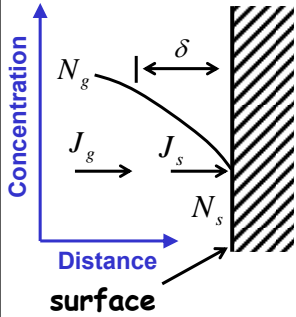
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## CVD Modeling

**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

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

$$J_g = \left( \frac{\bar{D}_g}{\delta} \right) (N_g - N_s) = h_g (N_g - N_s) \quad \text{Vapor phase mass-transfer coefficient}$$

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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

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)

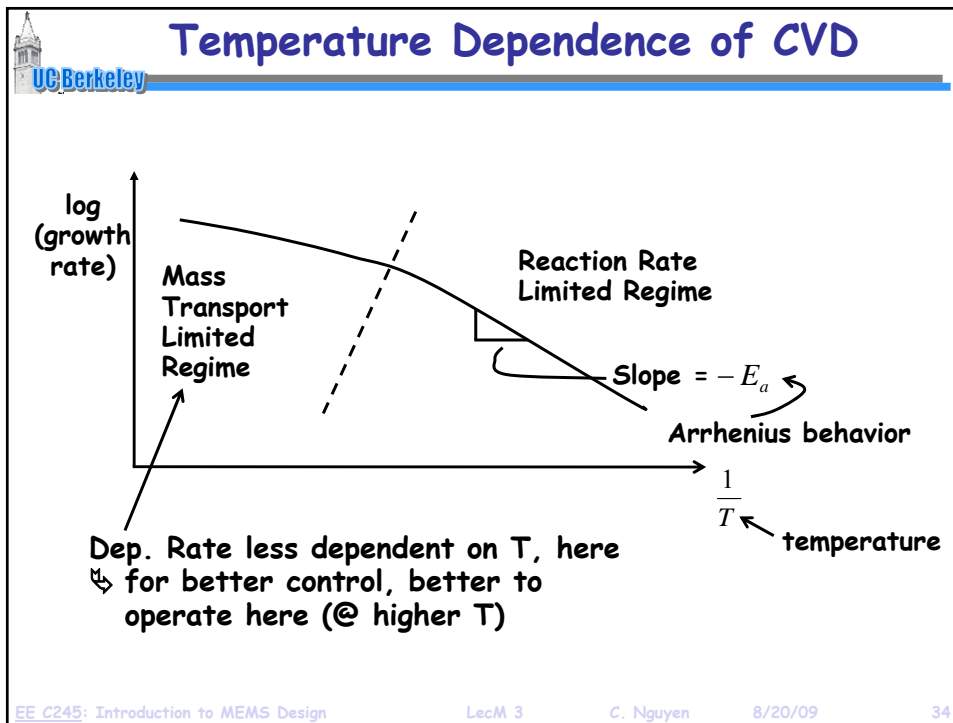
- **Case:**  $h_g \gg k_s$   
 ↳ mass transfer rate  $\gg$  surface reaction rate

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

(surface-reaction-limited)

$\sim R_0^{-E_a/kT}$  (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, Si<sub>3</sub>N<sub>4</sub>, SiO<sub>2</sub>, 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

Labels in diagram: Insulated RF input, Wafers, Glass cylinder, Aluminum electrodes, Plasma, Heated sample holder, Pump, Gas inlet.

- **Problems:**
  - ↪ Pin-holes
  - ↪ Non-stoichiometric films
  - ↪ Incorporation of  $H_2$ ,  $N_2$ ,  $O_2$  contaminants in film; can lead to outgassing or bubbling in later steps

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**Polysilicon CVD**

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**Polysilicon Deposition:**


$$SiH_4 \xrightarrow{600^\circ C} Si + 2H_2 \text{ (thermal decomposition of silane)}$$
 (conformal → high T)

LPCVD (25 to 150 Pa) → 100-200 Å/min

→ Fairly high temperature → conformal

- **In situ doping of polysilicon:**
  - ↪ n-type: add  $PH_3$  (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

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**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.)


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- 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.)

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

(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 NH<sub>3</sub> @ 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.)


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- Comments on LPCVD nitride films:
  - ↗ Hydrogen rich: ~8% H<sub>2</sub>
  - ↗ 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 (10<sup>16</sup> 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"> <li>↗ Non-stoichiometric nitride</li> <li>↗ 20-25% H<sub>2</sub> content</li> <li>↗ Can control stress</li> <li>↗ (10<sup>6</sup> Ω-cm) resistivity</li> </ul>
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43



## Metal CVD

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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 H<sub>2</sub>:

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

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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8/20/09
44

## 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<sub>4</sub>, SiH<sub>4</sub>, SiH<sub>2</sub>Cl<sub>2</sub> for vapor phase epitaxy.

SiCl<sub>4</sub>: Silicon tetrachloride  
 SiH<sub>4</sub>: silane  
 SiH<sub>4</sub>Cl<sub>2</sub>: 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!) ⇒ Reverse reaction (i.e., etching) if have excessive HCl → sometimes used before deposition to clean the Si wafer surface.

Also get a competing reaction.

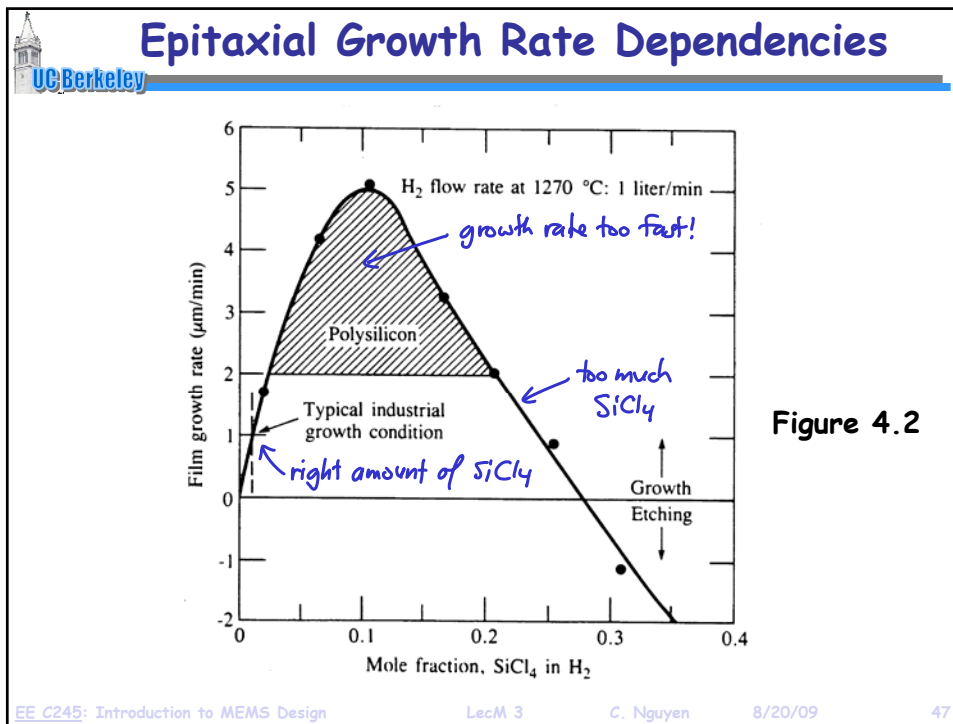
$$\text{SiCl}_4(\text{gas}) + \text{Si}(\text{solid}) \rightleftharpoons 2\text{SiCl}_2(\text{gas})$$

- ↳ Too much SiCl<sub>4</sub> → etching rather than growth takes place!
- ↳ Growth rate too fast → get polysilicon instead of Si. (> 2μm/min.)

} See Figure 4.2

**Important that the right conc. of SiCl<sub>4</sub> is used!**

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8/20/09
46



### 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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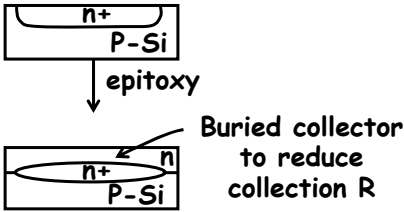


 **Doping of Epitaxial Layers**

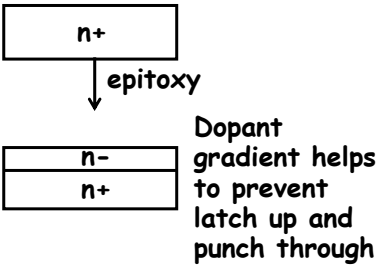
2. Use "autodoping" → when growing own heavily-doped substrates

- ↳ 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:**



**MOS:**



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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)**

• **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

Usually mixed w/ an inert gas to achieve lower effective vapor pressures → slows reaction, but needed to allow rapid pulsing & purging

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**Al<sub>2</sub>O<sub>3</sub> ALD**

The diagram shows a substrate surface (e.g., Si) with several silicon atoms (orange spheres) and hydrogen atoms (blue spheres). One silicon atom is bonded to an oxygen atom (red sphere), which is in turn bonded to a hydrogen atom, forming a hydroxyl group (OH). Above the surface, a Trimethyl aluminum (TMA) molecule, Al(CH<sub>3</sub>)<sub>3</sub>(g), is shown with an aluminum atom (purple sphere) bonded to three methyl groups (CH<sub>3</sub>), each consisting of a carbon atom (red sphere) and three hydrogen atoms (blue spheres). Labels indicate the TMA molecule, a methyl group (CH<sub>3</sub>), and the hydroxyl group (OH) from surface-adsorbed H<sub>2</sub>O.

- In air H<sub>2</sub>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

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**Al<sub>2</sub>O<sub>3</sub> ALD**

The diagram shows the reaction of TMA with the surface hydroxyl group. The TMA molecule is positioned above the hydroxyl group. An arrow labeled "Reaction of TMA with OH" points to the reaction site. Another arrow labeled "Methane reaction product CH<sub>4</sub>" points to a methane molecule (CH<sub>4</sub>) being released. The resulting surface species is a partially reacted TMA molecule, :Si-O-Al(CH<sub>3</sub>)<sub>2</sub>(s), where the aluminum atom is now bonded to two methyl groups and the oxygen atom of the surface hydroxyl group.

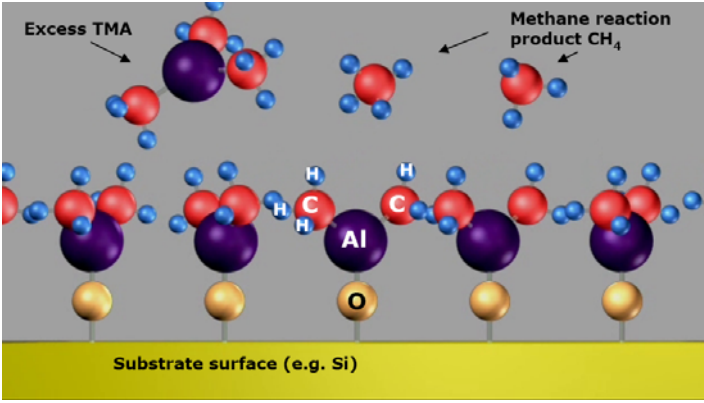
- TrimethylAluminum (TMA) reacts with the adsorbed hydroxyl groups, producing methane as the reaction product

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

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### Al<sub>2</sub>O<sub>3</sub> ALD



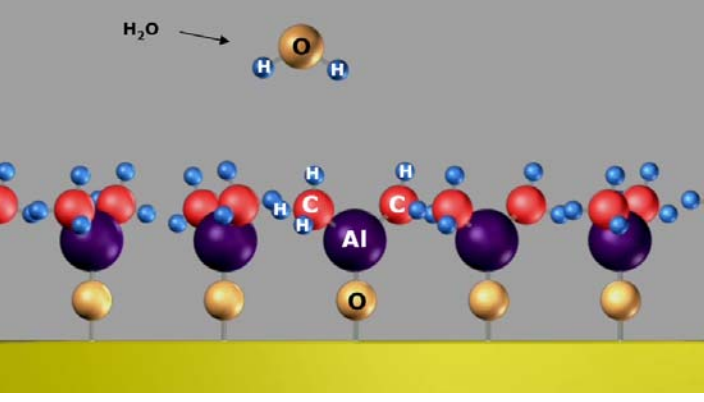
The diagram shows a substrate surface (e.g., Si) with a layer of adsorbed hydroxyl groups (OH). A TMA molecule (Al(CH<sub>3</sub>)<sub>3</sub>) is shown reacting with one of these hydroxyl groups. The reaction produces a surface-bound Al-CH<sub>3</sub> group and a methane molecule (CH<sub>4</sub>) as a byproduct. Excess TMA molecules are shown above the surface, and a methane molecule is shown being pumped away.

- 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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### Al<sub>2</sub>O<sub>3</sub> ALD



The diagram shows the substrate surface after the first step, with Al-CH<sub>3</sub> groups. A water vapor molecule (H<sub>2</sub>O) is shown reacting with one of these Al-CH<sub>3</sub> groups. The reaction produces a surface-bound Al-OH group and a methane molecule (CH<sub>4</sub>) as a byproduct.

- After the TMA and methane reaction product is pumped away, water vapor (H<sub>2</sub>O) is pulsed into the reaction chamber.

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**Al<sub>2</sub>O<sub>3</sub> ALD**

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- H<sub>2</sub>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

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

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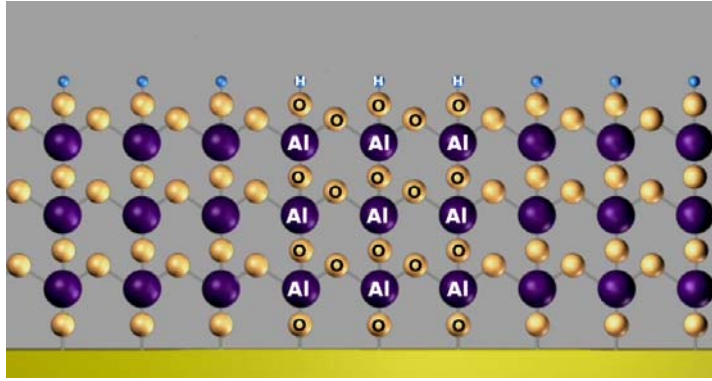
**Al<sub>2</sub>O<sub>3</sub> ALD**

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- The reaction product methane is pumped away
- Excess H<sub>2</sub>O vapor does not react with the hydroxyl surface groups
- Again, get perfect passivation to one atomic layer

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**Al<sub>2</sub>O<sub>3</sub> ALD**


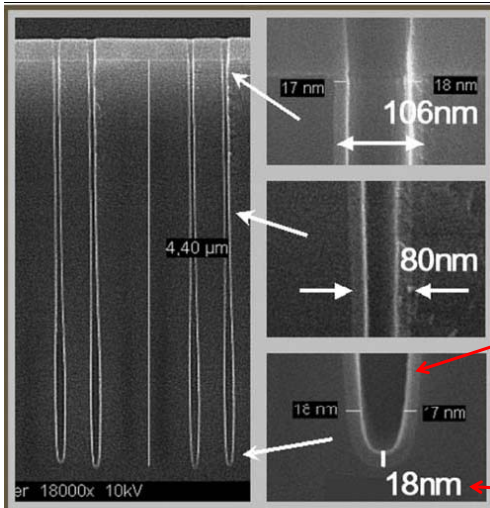
- One TMA and one H<sub>2</sub>O vapor pulse form one cycle
- Here, three cycles are shown, with approximately 1 Å per cycle
- Each cycle including pulsing and pumping takes, e.g., 3 sec

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

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

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**ALD Capability**

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

Al<sub>2</sub>O<sub>3</sub>

Figure 3. ALD features superb step coverage performance. The SEM images show close to 100% conformality for an 18nm thick Al<sub>2</sub>O<sub>3</sub> 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

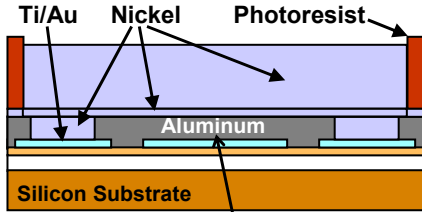
1. Switch on external supply of direct current
2. Metal at anode is oxidized to form cations with a (+) charge
3. Cations are attracted to the (-) charge on the cathode
4. Cations get reduced by  $e^-$ 's at the cathode, depositing the metal (in this case, Cu)

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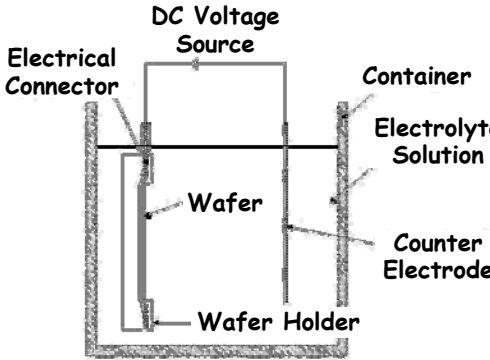
### Wafer-Level Implementation



- **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

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