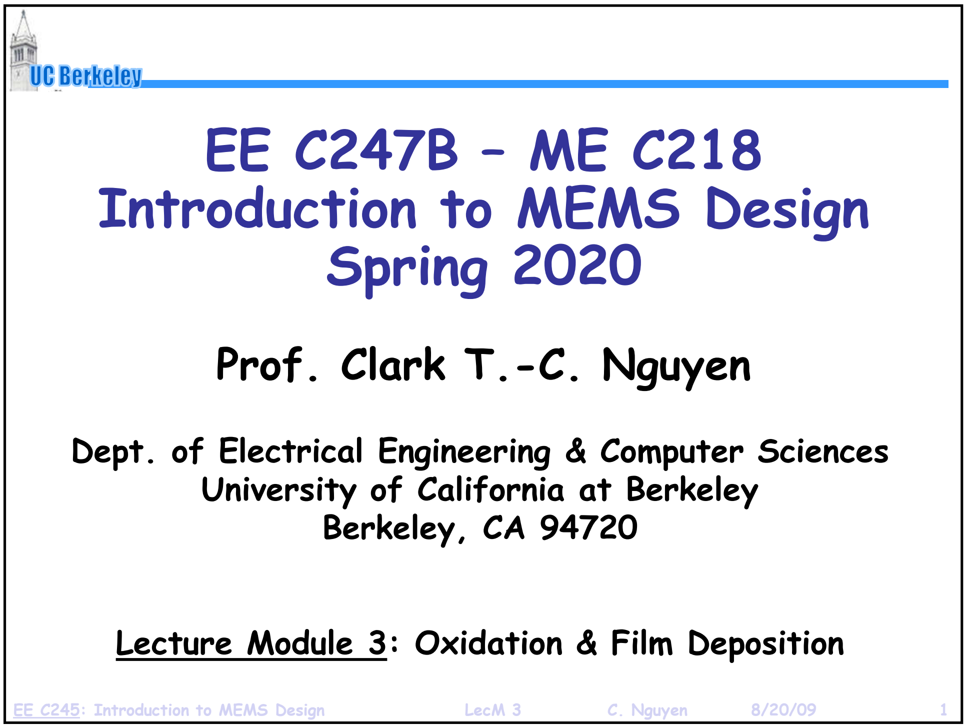

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EE C247B – ME C218
Introduction to MEMS Design
Spring 2020

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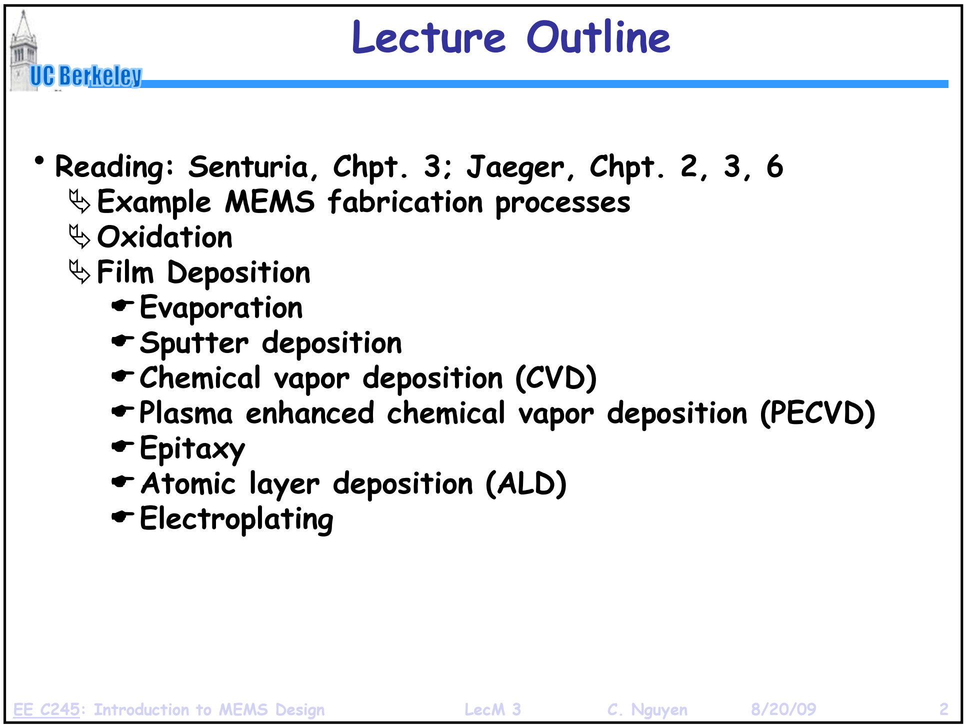
Lecture Module 3: Oxidation & Film Deposition



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Lecture Outline

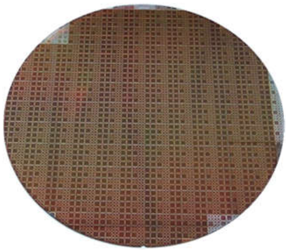
- Reading: Senturia, Chpt. 3; Jaeger, Chpt. 2, 3, 6
  - Example MEMS fabrication processes
  - Oxidation
  - Film Deposition
    - Evaporation
    - Sputter deposition
    - Chemical vapor deposition (CVD)
    - Plasma enhanced chemical vapor deposition (PECVD)
    - Epitaxy
    - Atomic layer deposition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

MEMS Fabrication

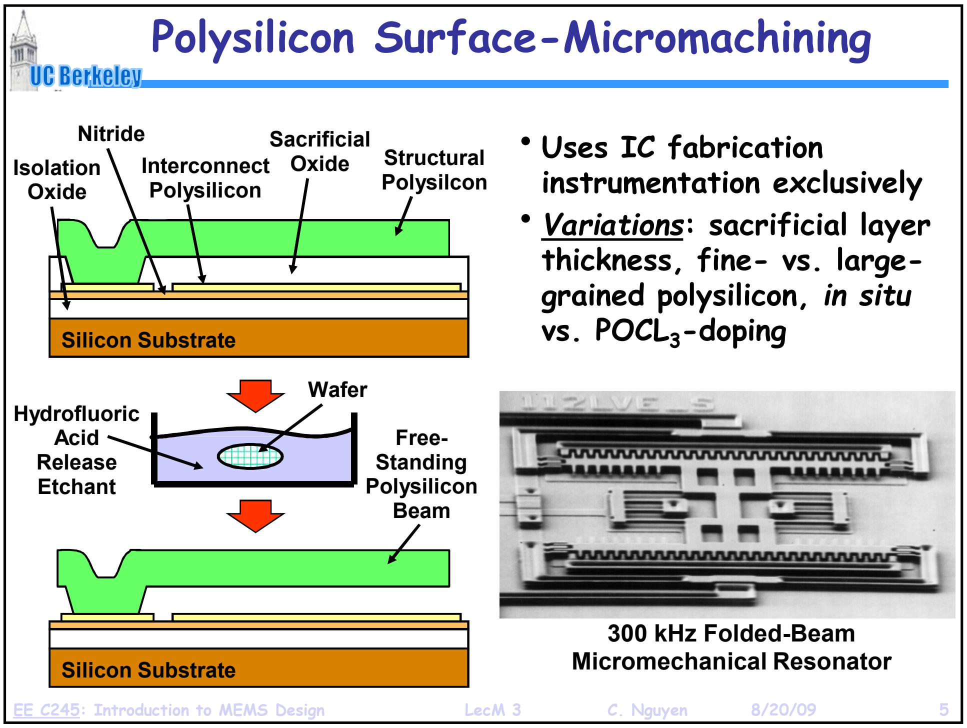
Making Mechanical Devices

- 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



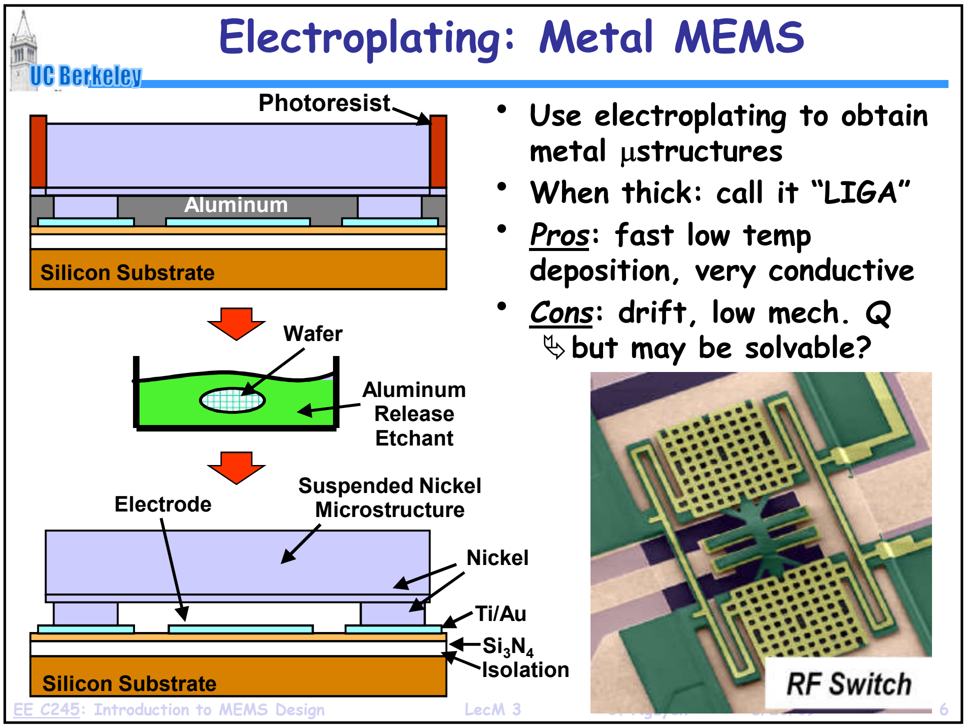
CMOS Integrated Circuit Wafer



Polysilicon Surface-Micromachining

- Uses IC fabrication instrumentation exclusively
- *Variations*: sacrificial layer thickness, fine- vs. large-grained polysilicon, *in situ* vs. $POCL_3$-doping

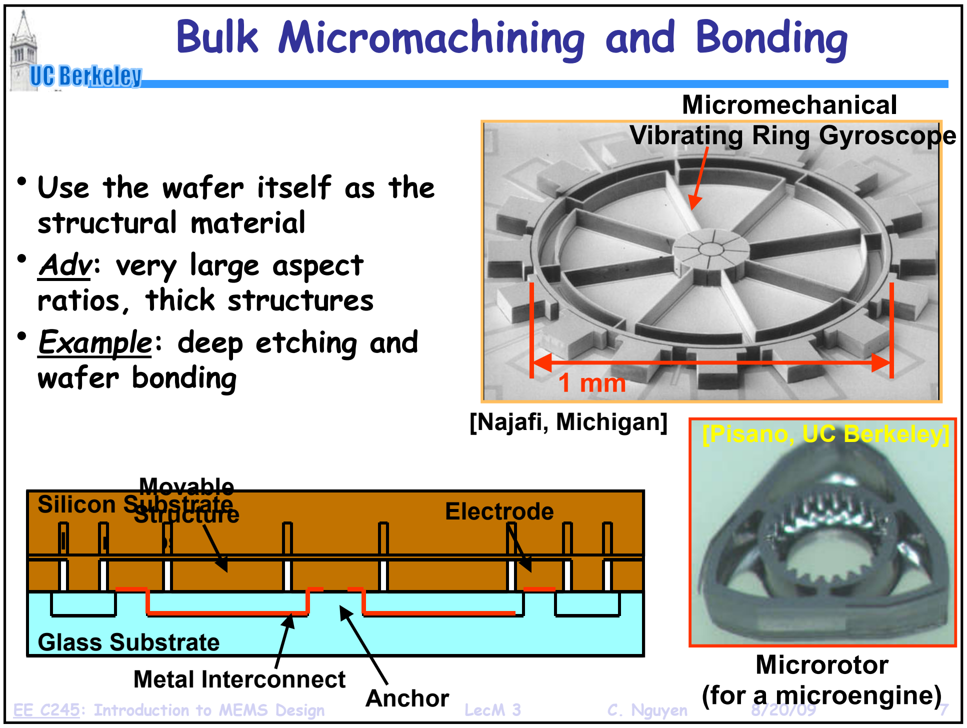
300 kHz Folded-Beam Micromechanical Resonator



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?

RF Switch



Bulk Micromachining and Bonding

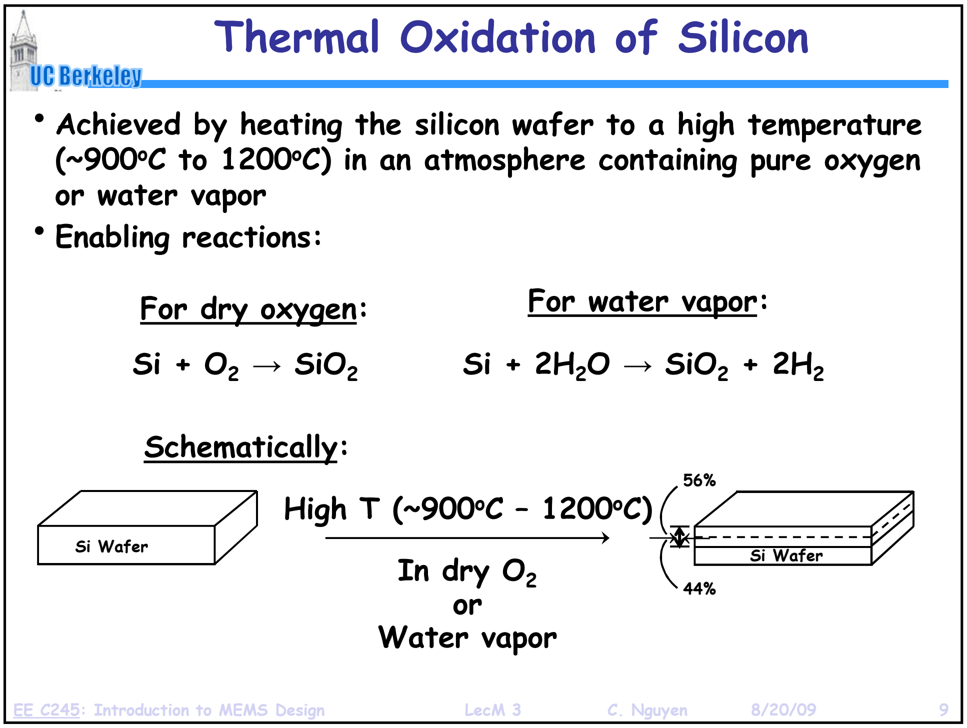
- Use the wafer itself as the structural material
- *Adv*: very large aspect ratios, thick structures
- *Example*: deep etching and wafer bonding

Micromechanical Vibrating Ring Gyroscope

[Najafi, Michigan]

Microrotor (for a microengine)

Oxidation



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:

<u>For dry oxygen</u>:

$Si + O_2 \rightarrow SiO_2$

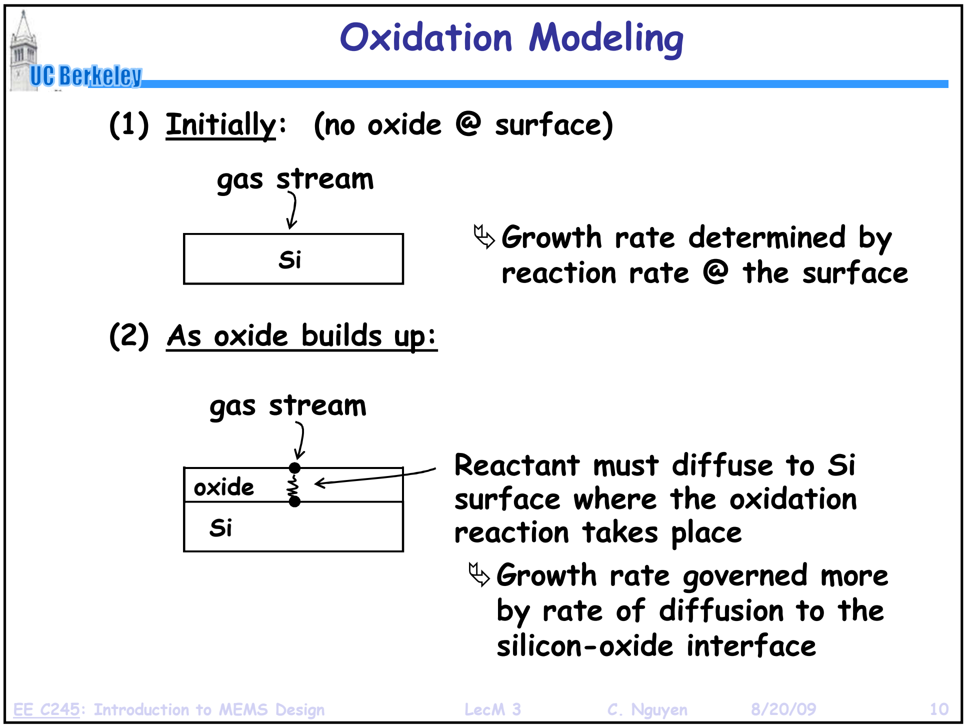
<u>For water vapor</u>:

$Si + 2H_2O \rightarrow SiO_2 + 2H_2$

<u>Schematically</u>:

$\xrightarrow{\text{High T (~900°C – 1200°C)}}$

In dry O_2
or
Water vapor



Oxidation Modeling

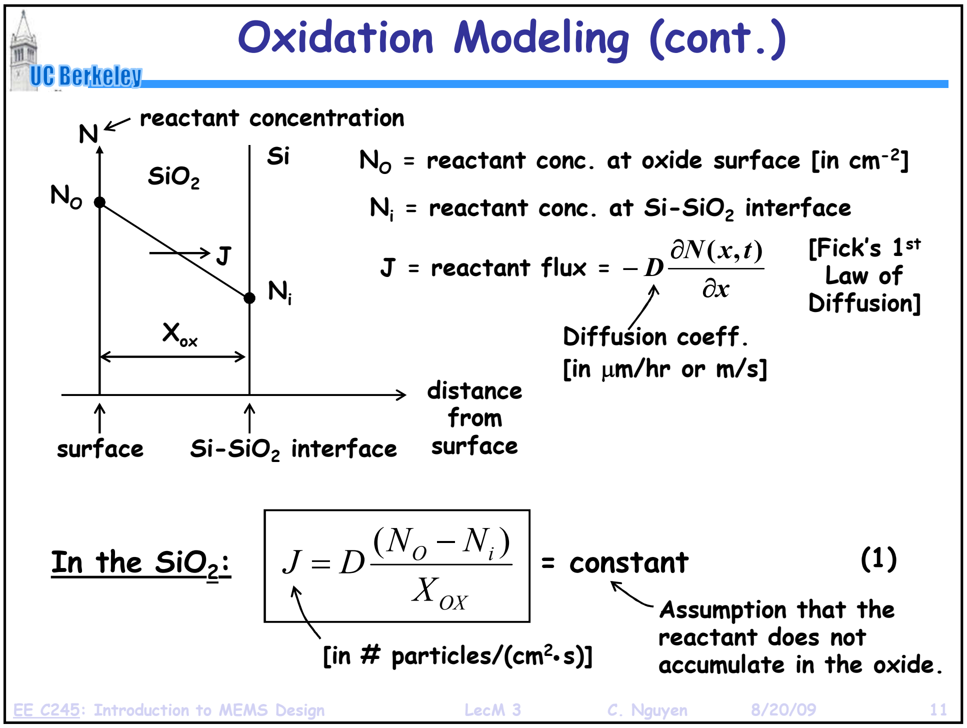
(1) <u>Initially</u>: (no oxide @ surface)

↳ Growth rate determined by reaction rate @ the surface

(2) <u>As oxide builds up:</u>

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



Oxidation Modeling (cont.)

N_O = reactant conc. at oxide surface [in cm^{-2}]

N_i = reactant conc. at Si-SiO$_2$ interface

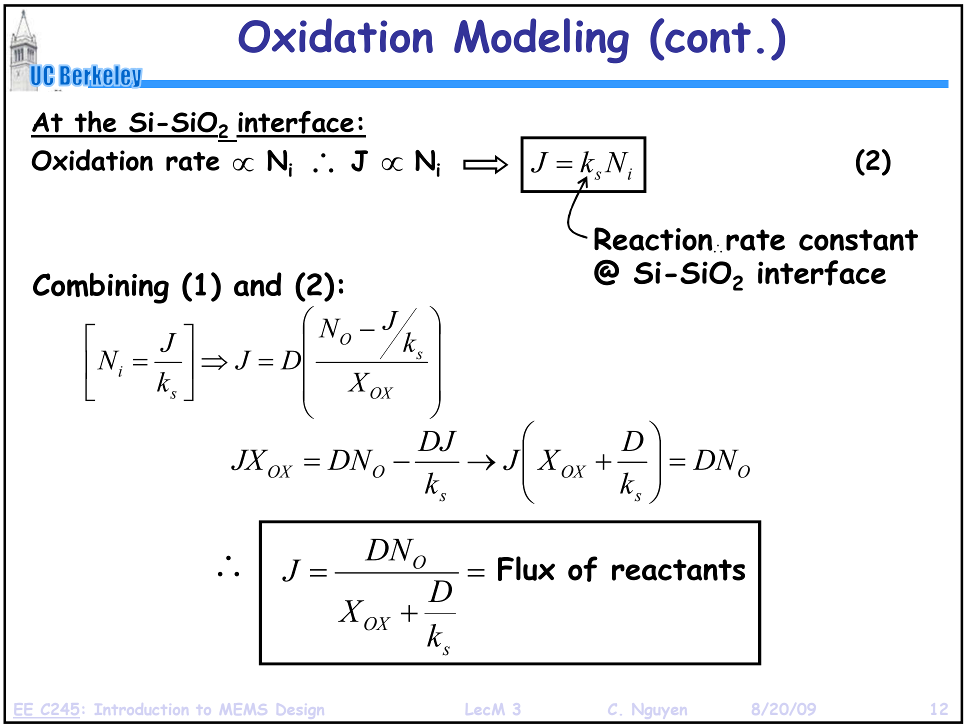
J = reactant flux = $-D\frac{\partial N(x,t)}{\partial x}$ [Fick's 1st Law of Diffusion]

Diffusion coeff. [in μm/hr or m/s]

In the SiO$_2$: $\boxed{J = D\frac{(N_O - N_i)}{X_{OX}}}$ = constant (1)

[in # particles/(cm^2•s)]

Assumption that the reactant does not accumulate in the oxide.



Oxidation Modeling (cont.)

At the Si-SiO$_2$ interface:

Oxidation rate ∝ N_i ∴ J ∝ N_i ⟹ $\boxed{J = k_s N_i}$ (2)

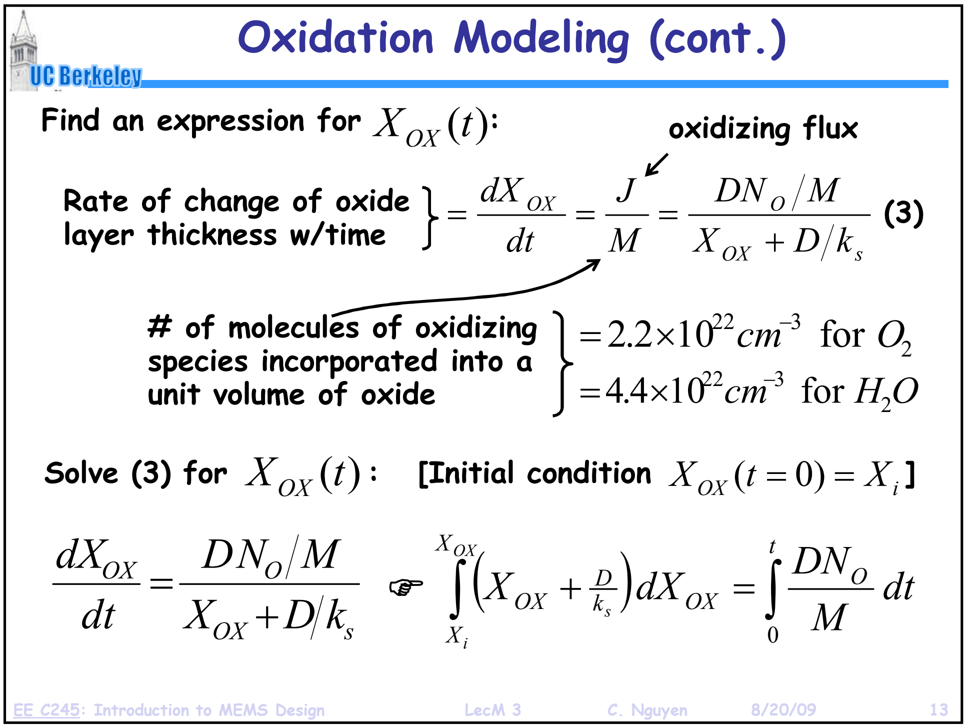
Reaction rate constant @ Si-SiO$_2$ interface

Combining (1) and (2):

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

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

$$\therefore \boxed{J = \frac{DN_O}{X_{OX} + \frac{D}{k_s}} = \text{Flux of reactants}}$$



Oxidation Modeling (cont.)

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

oxidizing flux

Rate of change of oxide layer thickness w/time

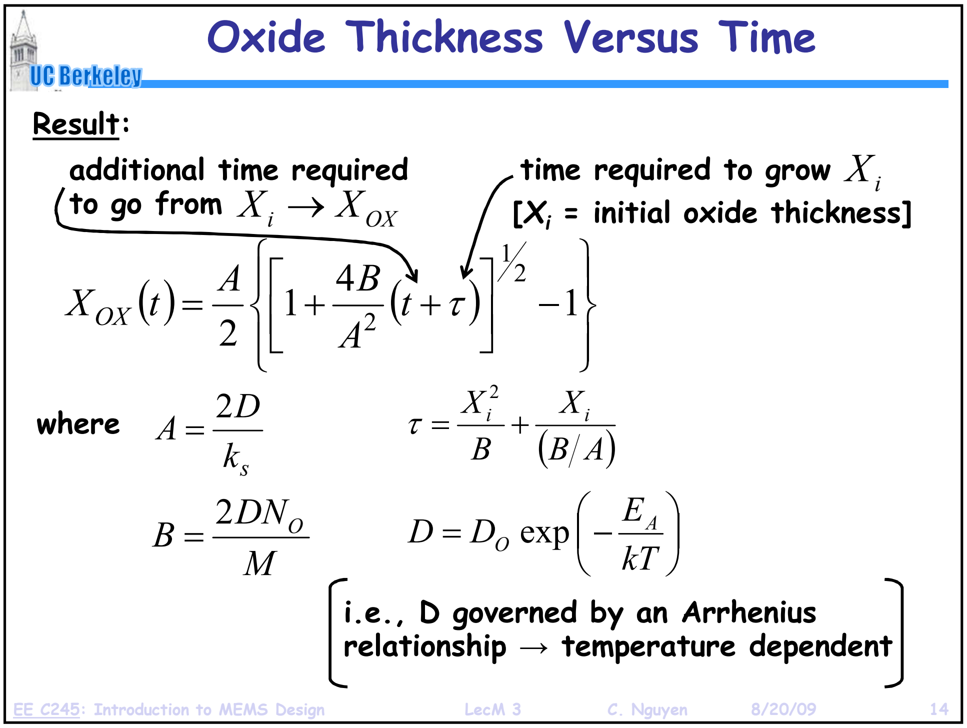
$$\left.\right\} = \frac{dX_{OX}}{dt} = \frac{J}{M} = \frac{DN_O/M}{X_{OX} + D/k_s} \quad \textbf{(3)}$$

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

$$\left.\right\} \begin{matrix} = 2.2\times10^{22} cm^{-3} \text{ for } O_2 \\ = 4.4\times10^{22} cm^{-3} \text{ for } H_2O \end{matrix}$$

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

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



Oxide Thickness Versus Time

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

$B = \dfrac{2DN_O}{M}$ $\qquad D = D_O \exp\left(-\dfrac{E_A}{kT}\right)$

i.e., D governed by an Arrhenius relationship → temperature dependent

Oxidation Modeling (cont.)

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For shorter times:

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

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

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

$t >> \tau$

Parabolic rate constant

Oxidation Rate Constants

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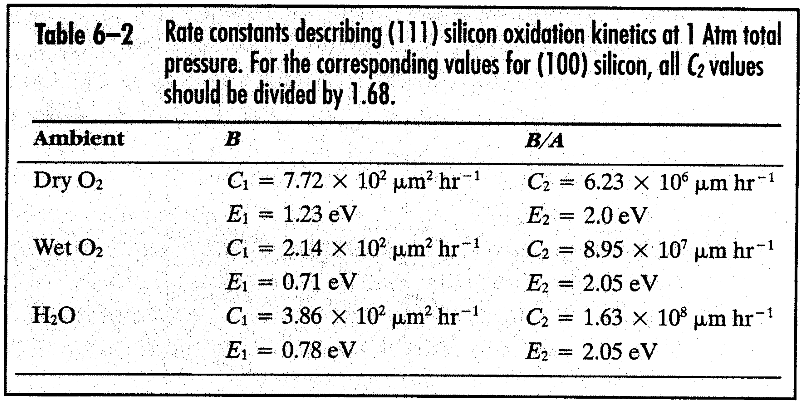
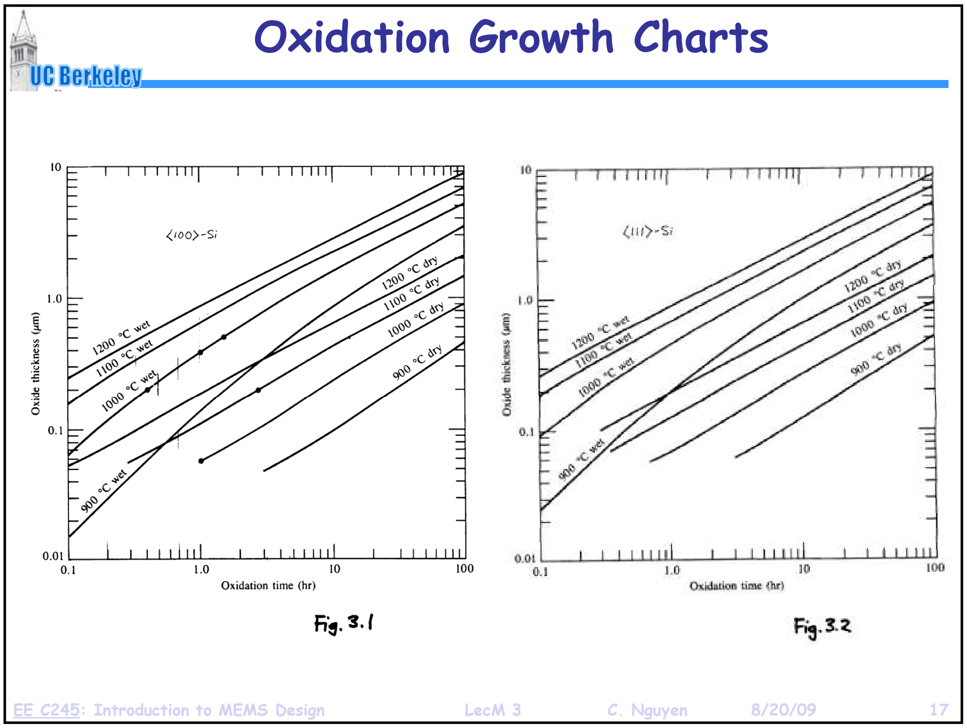


Table 6–2 Rate constants describing (111) silicon oxidation kinetics at 1 Atm total pressure. For the corresponding values for (100) silicon, all C_2 values should be divided by 1.68.

Ambient	B	B/A
Dry O_2	$C_1 = 7.72 \times 10^2\ \mu m^2\ hr^{-1}$	$C_2 = 6.23 \times 10^6\ \mu m\ hr^{-1}$
	$E_1 = 1.23$ eV	$E_2 = 2.0$ eV
Wet O_2	$C_1 = 2.14 \times 10^2\ \mu m^2\ hr^{-1}$	$C_2 = 8.95 \times 10^7\ \mu m\ hr^{-1}$
	$E_1 = 0.71$ eV	$E_2 = 2.05$ eV
H_2O	$C_1 = 3.86 \times 10^2\ \mu m^2\ hr^{-1}$	$C_2 = 1.63 \times 10^8\ \mu m\ hr^{-1}$
	$E_1 = 0.78$ eV	$E_2 = 2.05$ 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



Oxidation Growth Charts

Fig. 3.1

Fig. 3.2

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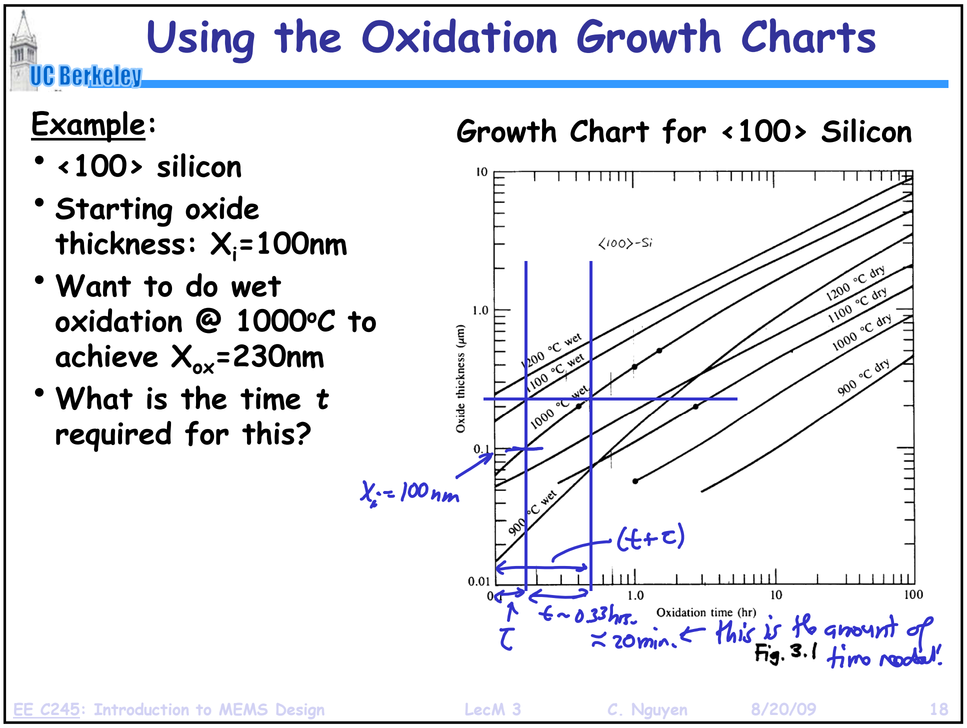

Using the Oxidation Growth Charts

Example:

- <100> silicon
- Starting oxide thickness: X_i=100nm
- Want to do wet oxidation @ 1000°C to achieve X_{ox}=230nm
- What is the time t required for this?

Growth Chart for <100> Silicon

← this is the amount of time needed!

Fig. 3.1

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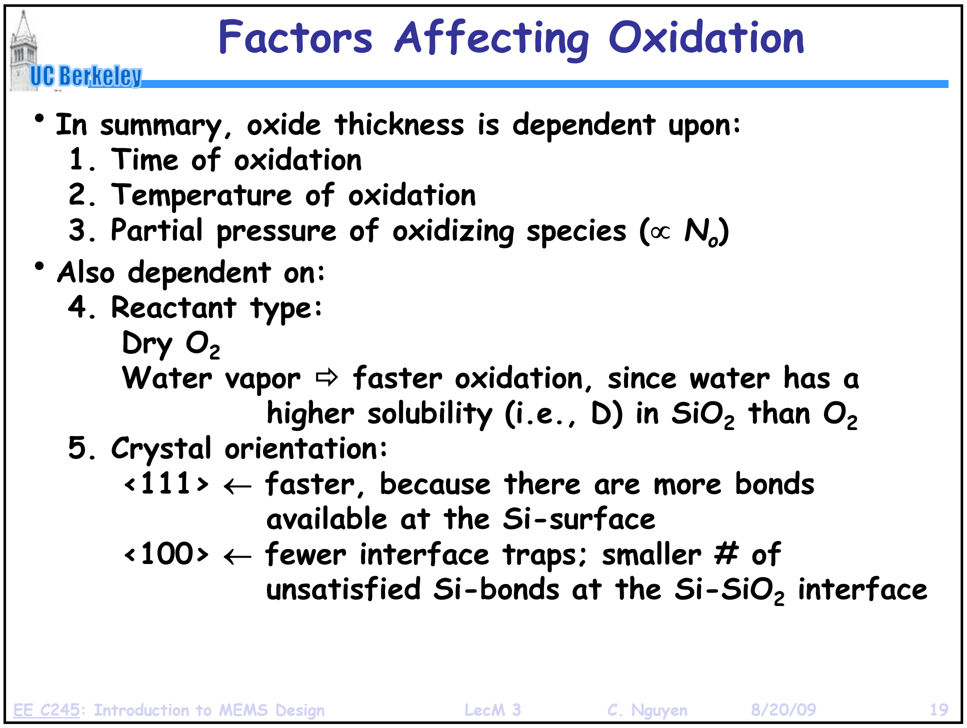
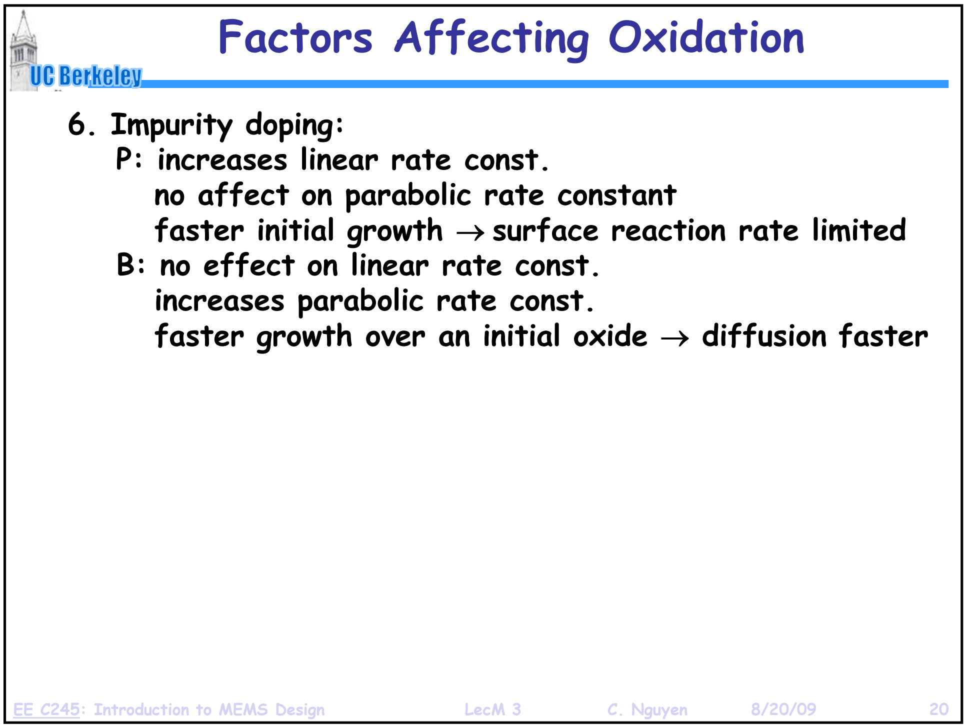


Factors Affecting Oxidation

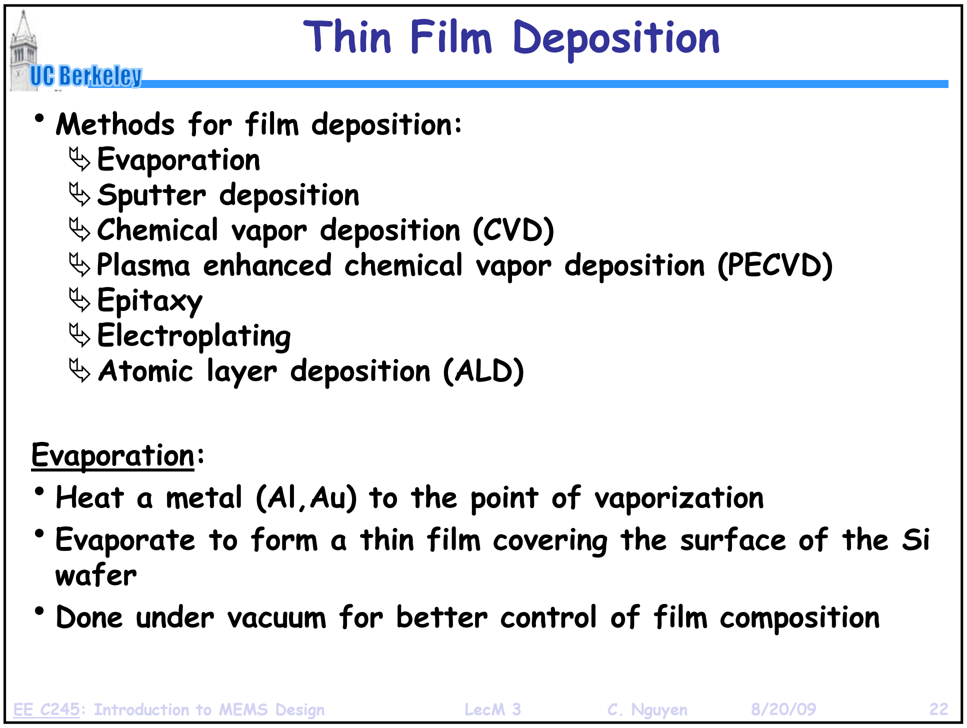
- In summary, oxide thickness is dependent upon:
  1. Time of oxidation
  2. Temperature of oxidation
  3. Partial pressure of oxidizing species ($\propto N_o$)
- Also dependent on:
  4. Reactant type:
     Dry O_2
     Water vapor ⇨ faster oxidation, since water has a higher solubility (i.e., D) in SiO_2 than O_2
  5. Crystal orientation:
     <111> ← faster, because there are more bonds available at the Si-surface
     <100> ← fewer interface traps; smaller # of unsatisfied Si-bonds at the Si-SiO_2 interface



Factors Affecting Oxidation

6. Impurity doping:
   P: increases linear rate const.
   no affect on parabolic rate constant
   faster initial growth → surface reaction rate limited
   B: no effect on linear rate const.
   increases parabolic rate const.
   faster growth over an initial oxide → diffusion faster

Thin Film Deposition

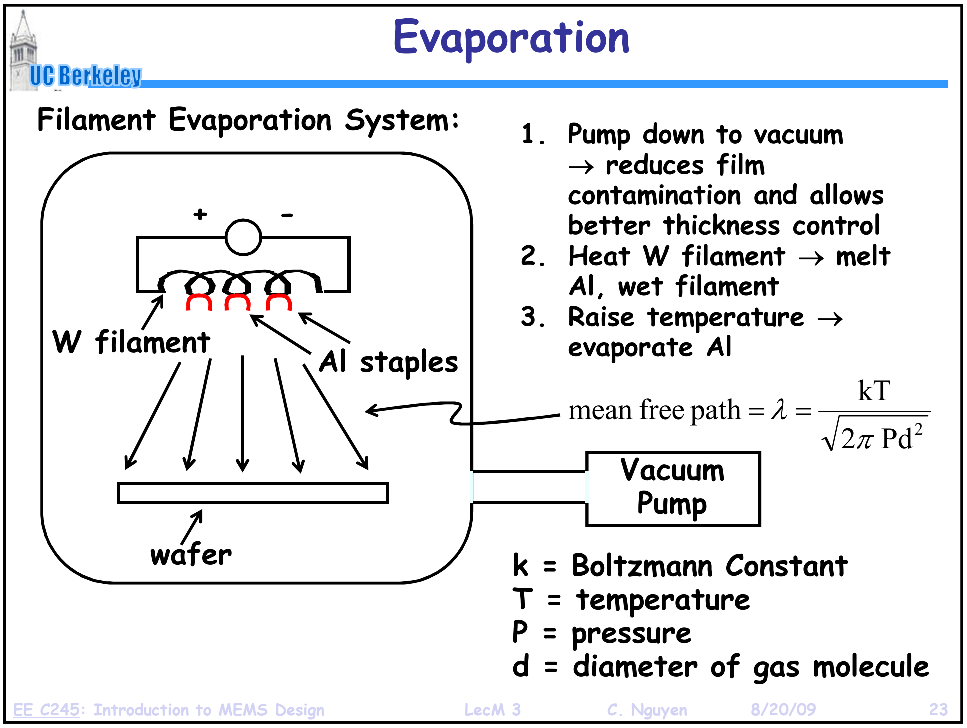


Thin Film Deposition

- 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



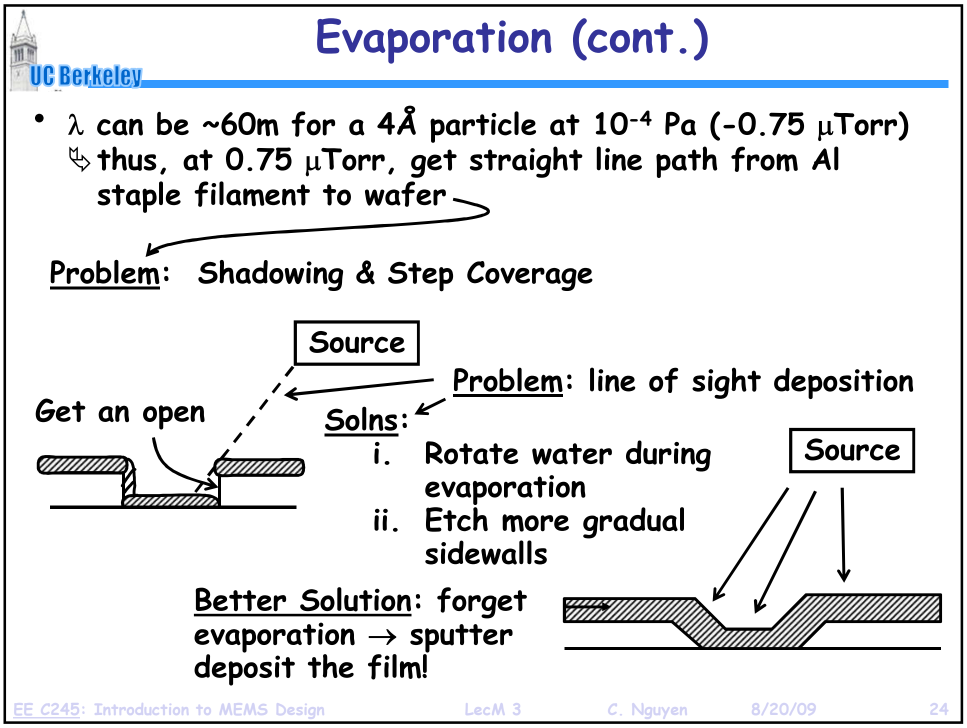
Evaporation

Filament Evaporation System:

1. Pump down to vacuum → 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



Evaporation (cont.)

- λ can be ~60m for a 4Å particle at 10^{-4} Pa (-0.75 μTorr)
  ↳ thus, at 0.75 μTorr, get straight line path from Al staple filament to wafer

Problem: Shadowing & Step Coverage

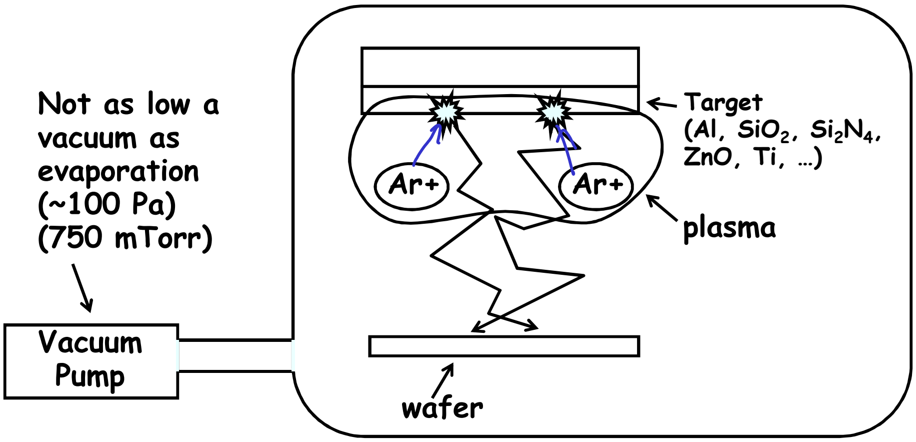
Problem: line of sight deposition

Solns:
i. Rotate water during evaporation
ii. Etch more gradual sidewalls

Better Solution: forget evaporation → 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



Sputter Deposition Process

- Step-by-step procedure:
  1. Pump down to vacuum

$$(\sim 100\ \text{Pa}) \rightarrow 1\ \text{Pa} = 9.8\times10^{-6}\ \text{atm}\left(\frac{760\ \text{Torr}}{\text{atm}}\right) = 0.0075012\ \text{Torr}$$

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, λ ~60μm 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)

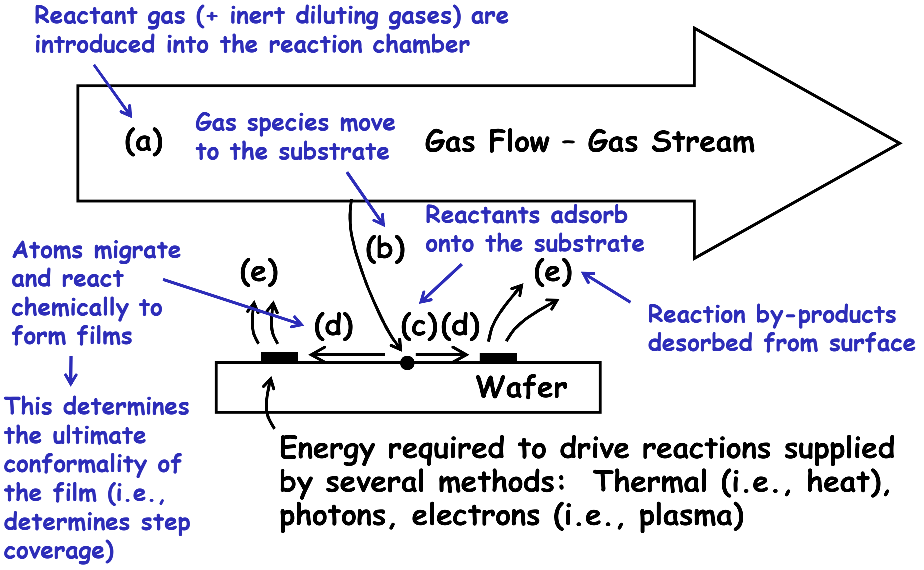
Chemical Vapor Deposition (CVD)

- 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 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), …

The CVD Process



Energy required to drive reactions supplied by several methods: Thermal (i.e., heat), photons, electrons (i.e., plasma)

The CVD Process (cont.)

Step-by-Step CVD Sequence:

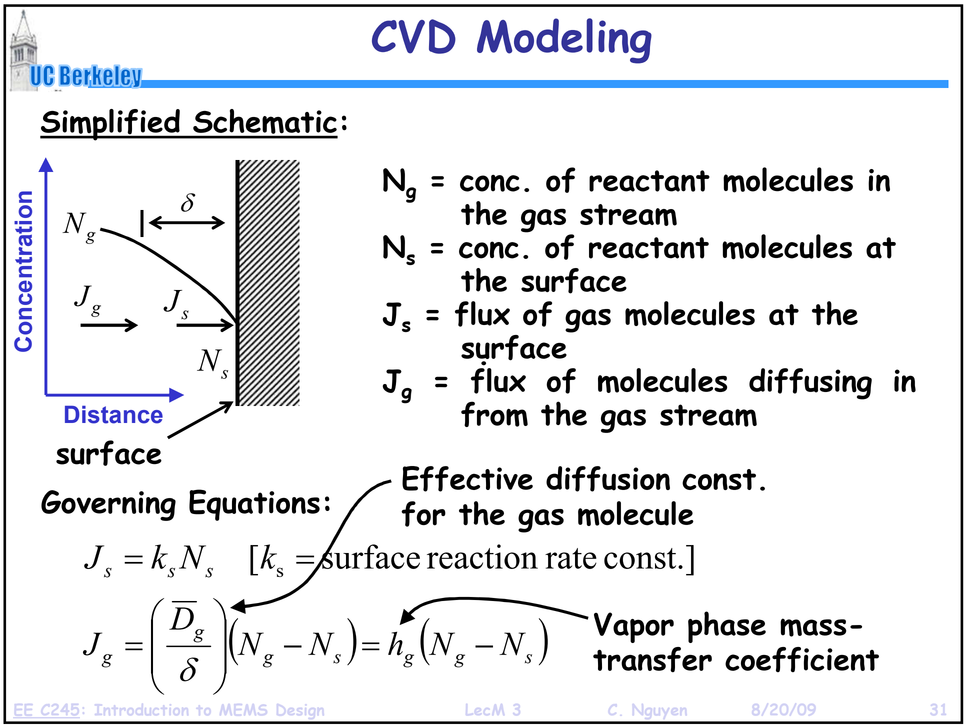
Gas phase processes
- a) Reactant gases (+ inert diluting gases) are introduced into reaction chamber
- b) Gas species move to the substrate

Surface processes
- c) Reactants adsorbed onto the substrate
- d) Atoms migrate and react chemically to form films
  This determines to a large extent whether or not a film is conformal (i.e. better step coverage)

Not Conformal
low T
not enough adatom migration

Conformal
High T
Plenty of adatom migration

- e) Reaction by-products desorbed and removed from reaction chamber



CVD Modeling

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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

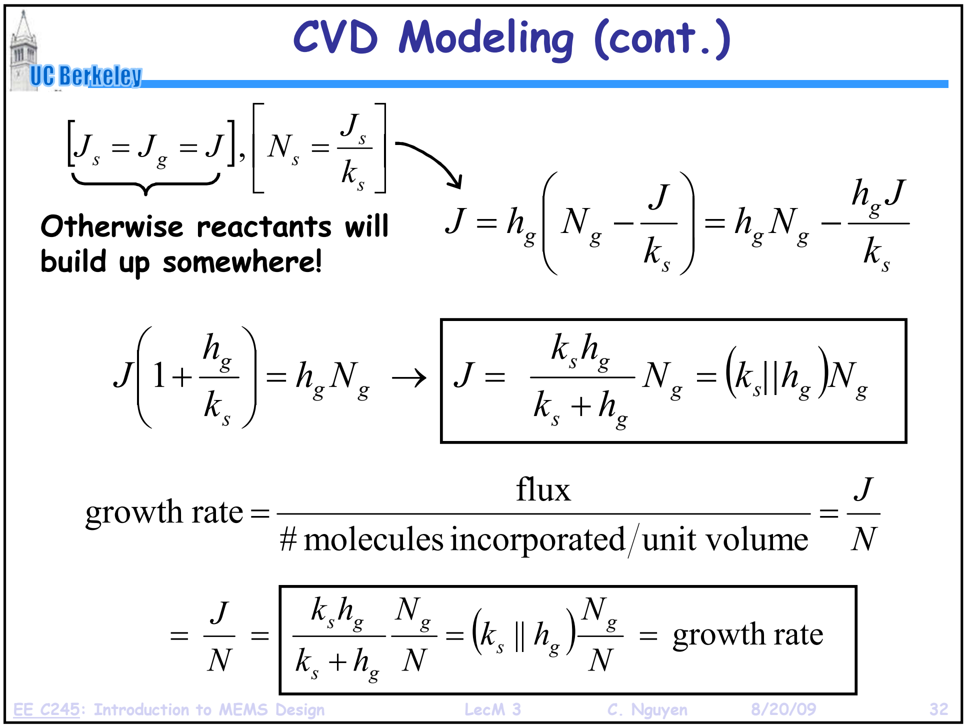
Governing Equations:

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

Effective diffusion const. for the gas molecule

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

Vapor phase mass-transfer coefficient



CVD Modeling (cont.)

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

Otherwise reactants will build up somewhere!

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

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

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

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

CVD Modeling (cont.)

- Case: $k_s >> h_g$
  ↳ surface reaction rate >> mass transfer rate

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

(mass-transfer-limited)

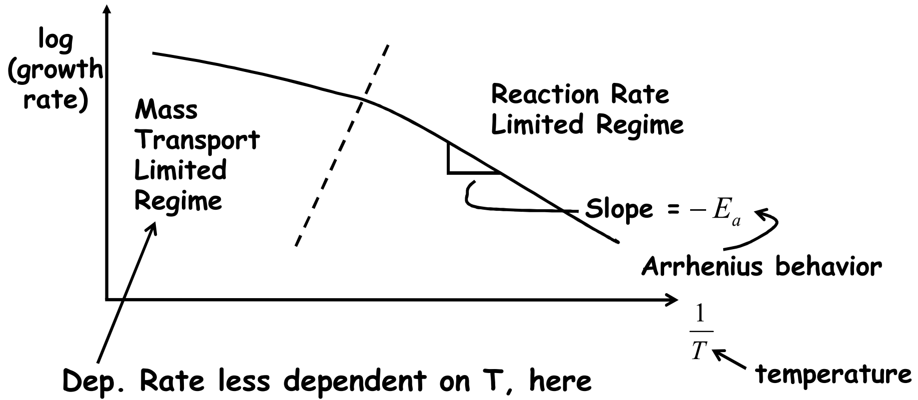
- Case: $h_g >> k_s$
  ↳ mass transfer rate >> surface reaction rate

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

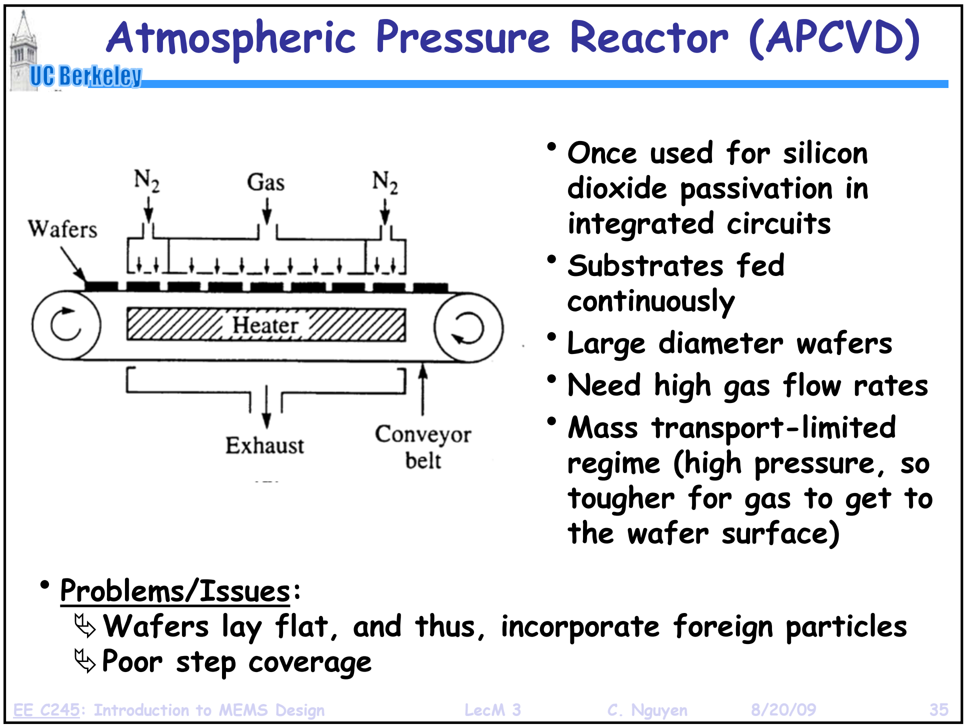
(surface-reaction-limited)

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

Temperature Dependence of CVD



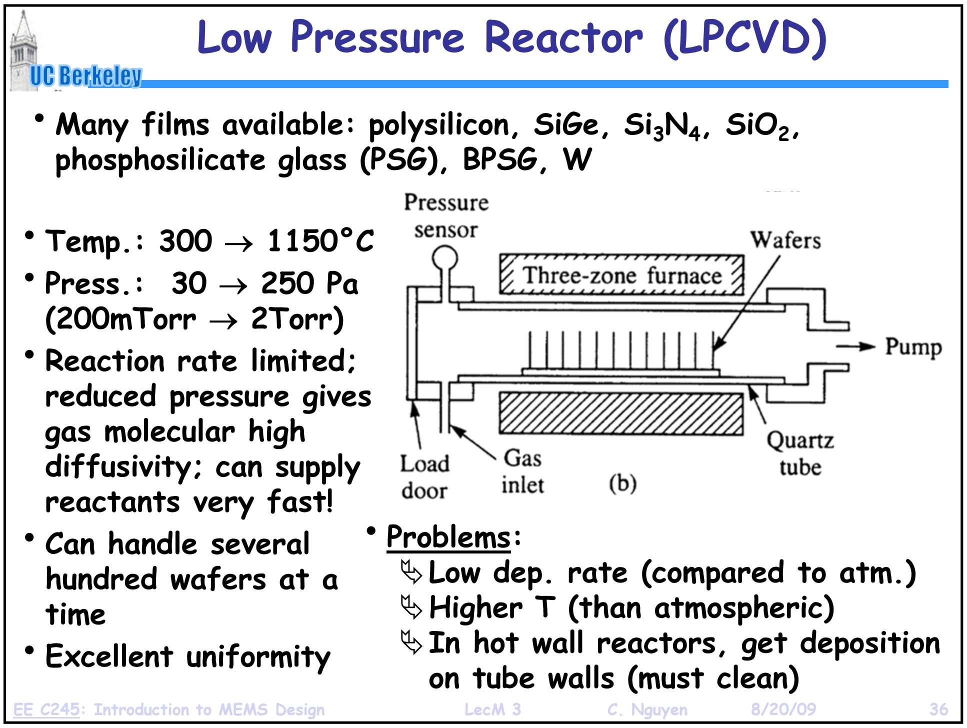
Dep. Rate less dependent on T, here
↳ for better control, better to operate here (@ higher T)



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)

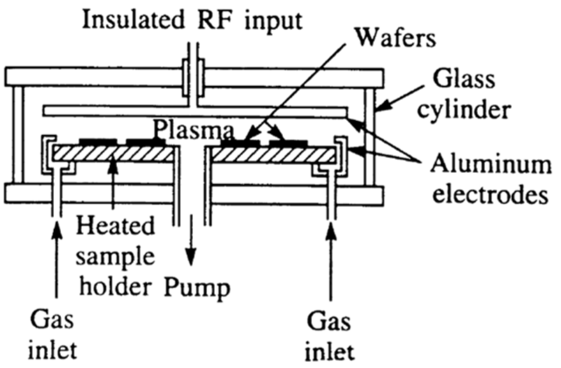
- Many films available: polysilicon, SiGe, Si_3N_4, SiO_2, phosphosilicate glass (PSG), BPSG, W

- 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_2, N_2, O_2 contaminants in film; can lead to outgassing or bubbling in later steps

Polysilicon CVD

Polysilicon Deposition:

→ Fairly high temperature → conformal

$$SiH_4 \xrightarrow{600°C} Si + 2H_2$$ (thermal decomposition of silane)

(conformal ⟶ high T)

LPCVD (25 to 150 Pa) → 100-200Å/min

- In situ doping of polysilicon:
  - ↳ n-type: add PH_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:

$$\text{LPCVD LTO Reactions}\begin{cases} \underset{\text{(silane)}}{SiH_4} + O_2 \xrightarrow[300\text{-}500^\circ C]{} SiO_2 + 2H_2 \\ \underset{\text{(phosphine)}}{4PH_3} + 5O_2 \xrightarrow[300\text{-}500^\circ C]{} 2P_2O_5 + 6H_2 \end{cases}$$

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

$$\text{HTO}\begin{cases} \underset{\text{(dichlorosilane)}}{SiCl_2H_2} + \underset{\text{(Nitrous oxide)}}{2N_2O} \xrightarrow[\sim 900^\circ C]{} \underset{\text{(nice conformal step coverage)}}{SiO_2 + 2N_2 + 2HCl} \end{cases}$$

or …

Silicon Oxide CVD (cont.)

$$Si(OC_2H_5)_4 \xrightarrow[650\text{-}750°C]{} SiO_2 + \text{by-products}$$

(Tetraethylorthosilicate)
(TEOS)

(excellent uniformity &
conformal step coverage)

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:

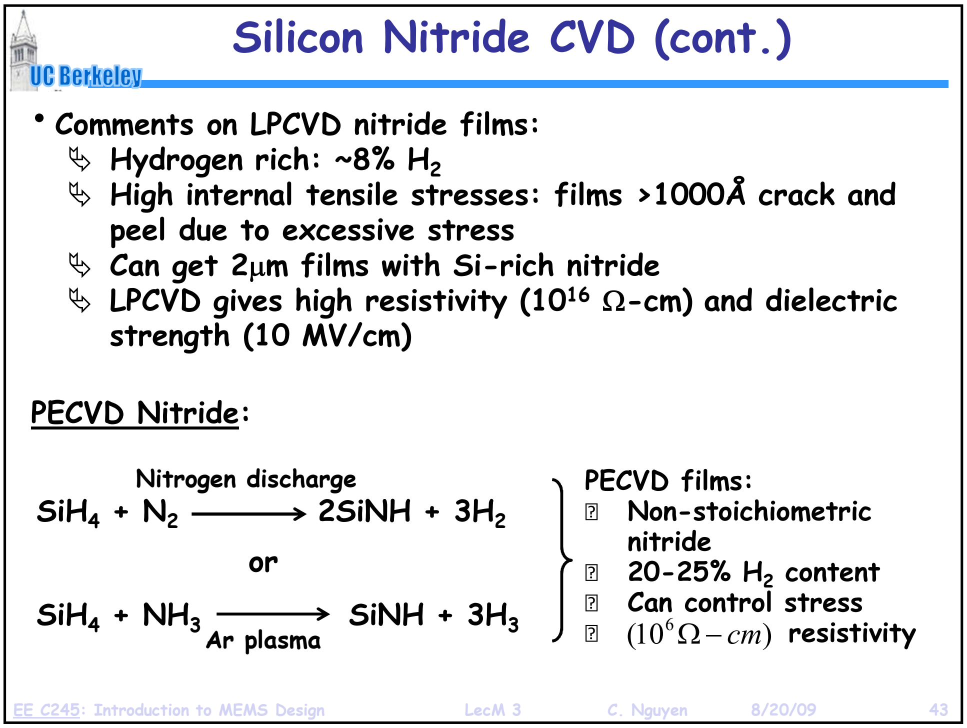
Silane reaction: $$3SiH_4 + 4NH_3 \xrightarrow[\text{(Atm. Press.)}]{700\text{-}900°C} Si_3N_4 + 12H_2$$

Dichlorosilane reaction:

$$3SiCl_2H_2 + 4NH_3 \xrightarrow[\text{(LPCVD)}]{700\text{-}800°C} Si_3N_4 + 6HCl + 6H_2$$

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% H_2
  - 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^{16} Ω-cm) and dielectric strength (10 MV/cm)

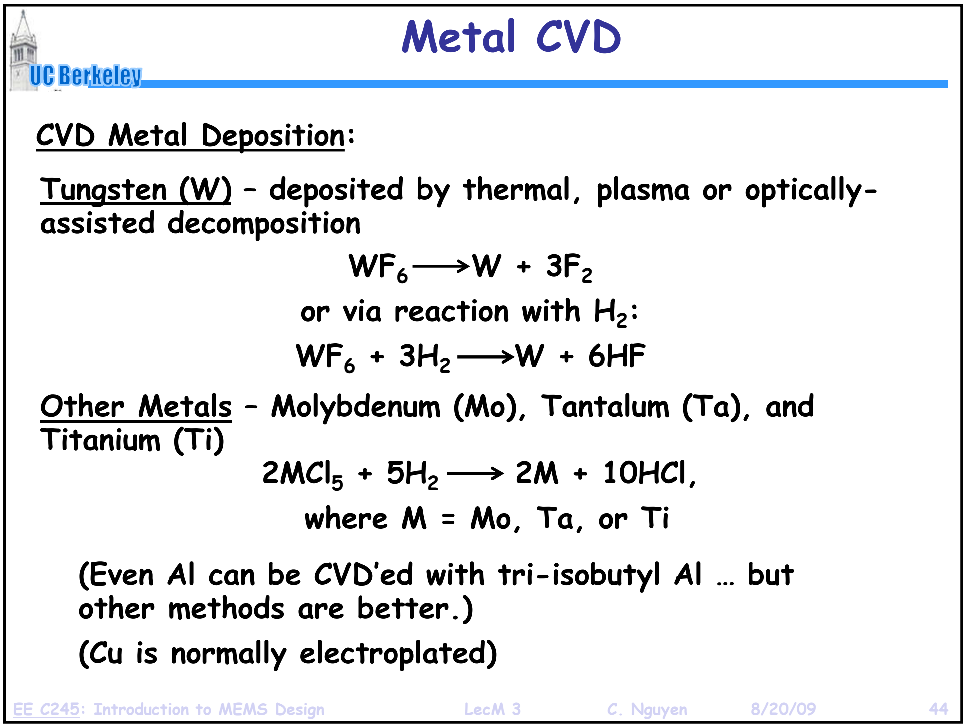
PECVD Nitride:

$$SiH_4 + N_2 \xrightarrow{\text{Nitrogen discharge}} 2SiNH + 3H_2$$

or

$$SiH_4 + NH_3 \xrightarrow[\text{Ar plasma}]{} SiNH + 3H_3$$

PECVD films:
- Non-stoichiometric nitride
- 20-25% H_2 content
- Can control stress
- $(10^6 \Omega - cm)$ resistivity



Metal CVD

CVD Metal Deposition:

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

$$WF_6 \longrightarrow W + 3F_2$$

or via reaction with H_2:

$$WF_6 + 3H_2 \longrightarrow W + 6HF$$

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

$$2MCl_5 + 5H_2 \longrightarrow 2M + 10HCl,$$

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)

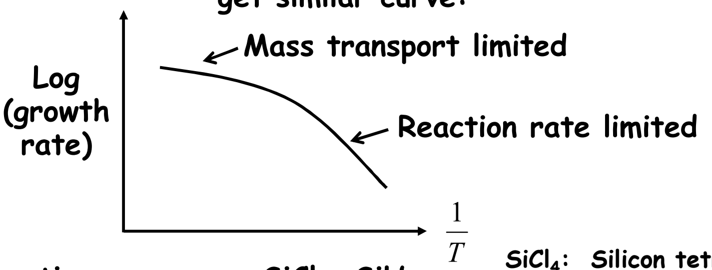
Epitaxy

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_4Cl_2: dichlorosilane

Epitaxy (cont.)

Most popular: $SiCl_4\,(gas) + 2H_2\,(gas) \xrightarrow{1200°C} Si\,(solid) + 4HCl\,(gas)$

(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.

$SiCl_4\,(gas) + Si\,(solid) \longleftrightarrow 2SiCl_2\,(gas)$

- ➩ Too much $SiCl_4$ → 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 $SiCl_4$ is used!

Epitaxial Growth Rate Dependencies

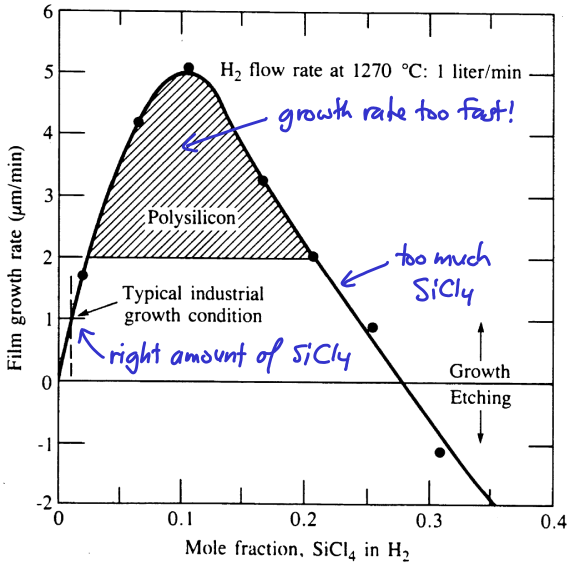


Figure 4.2

Epitaxy (cont.)

Alternative reaction: pyrolytic decomposition of silane:

$$SiH_4 \xrightarrow{650°C} Si + 2H_2$$

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:

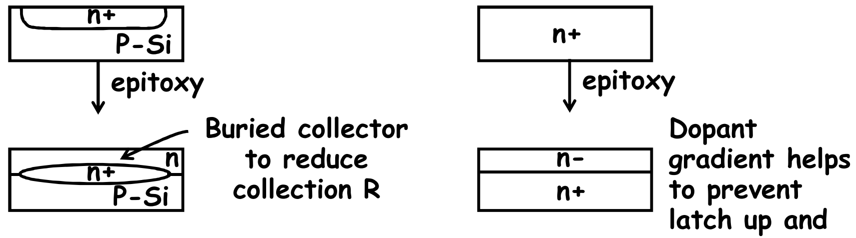
1. Just add impurities during growth: Arsine, diborane, Phosphine
   ↳ Control resistivity by varying partial pressure of dopant species
      i. Arsine, Phosphine → slow down the growth rate
      ii. Diborane → enhances growth rate

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:

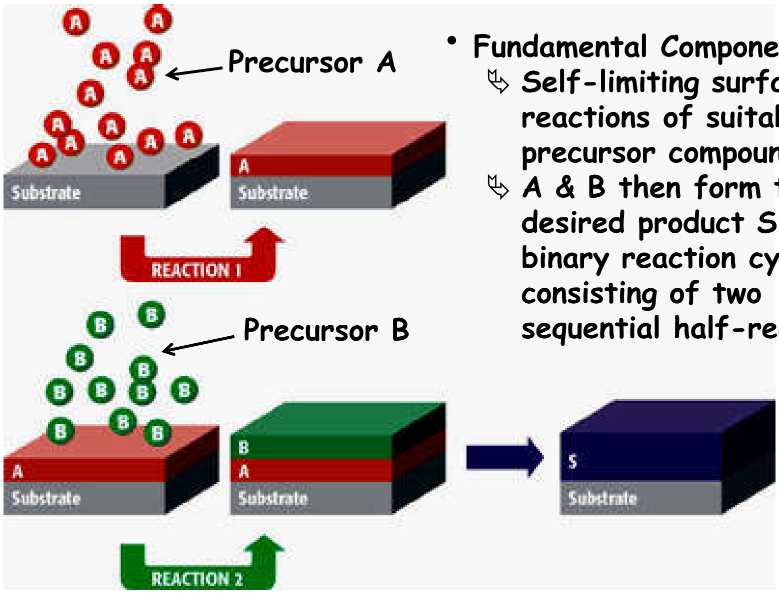


Buried collector to reduce collection R

Dopant gradient helps to prevent latch up and punch through

Atomic Layer Deposition (ALD)

Atomic Layer Deposition (ALD)



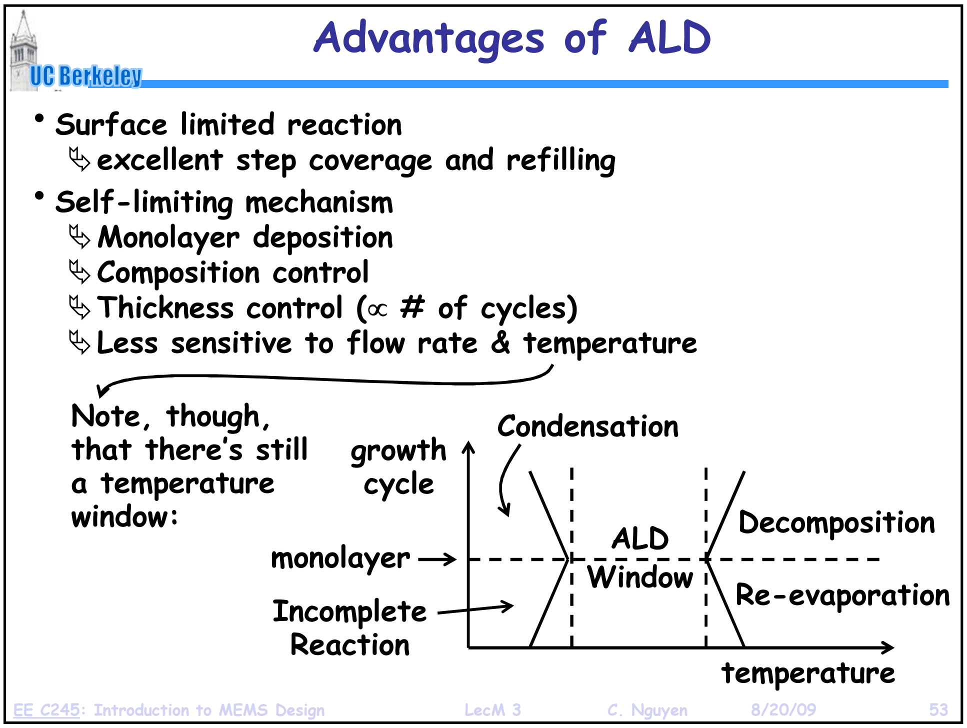
- Fundamental Components:
  - ↳ Self-limiting surface reactions of suitable precursor compounds A & B
  - ↳ A & B then form the desired product S in a binary reaction cycle consisting of two sequential half-reactions

Atomic Layer Deposition (ALD)

- **Remarks**:
  - ↳ Both half-reactions must be *complete* and *self-limiting* at the monolayer level
  - ↳ The total film thickness d(tot) can be "digitally" controlled by the number of applied deposition cycles N(A/B):

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

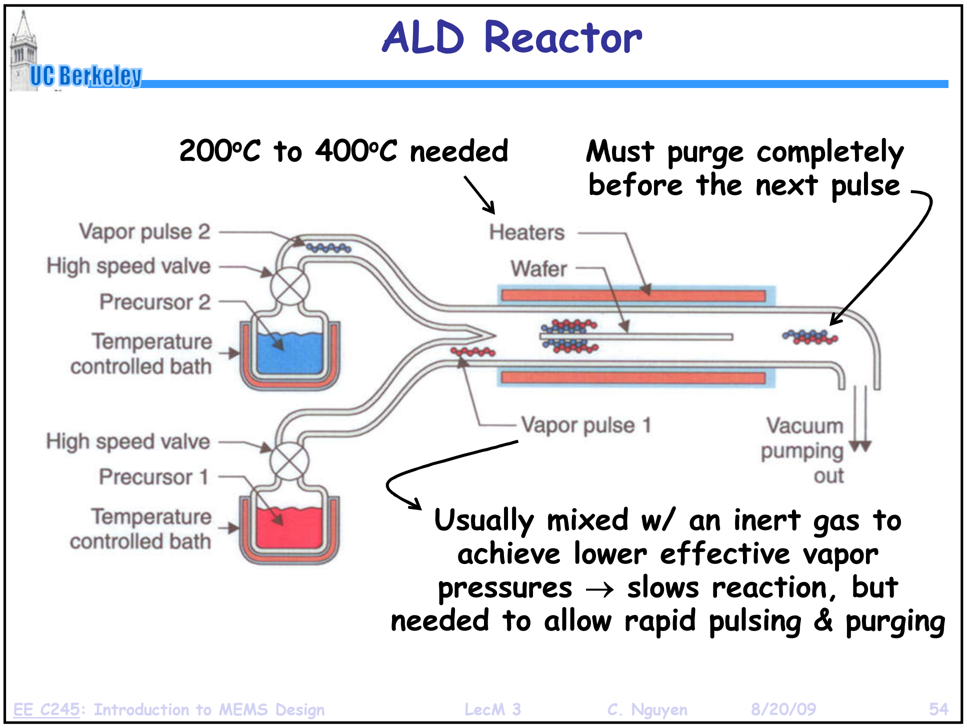
  - ↳ The reagents A & B in the half reactions are normally chemical reactions
    - ☛ But they don't need to be
    - ☛ They can also represent a physical process, e.g., heating, irradiation, electrochemical conversion



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 window:

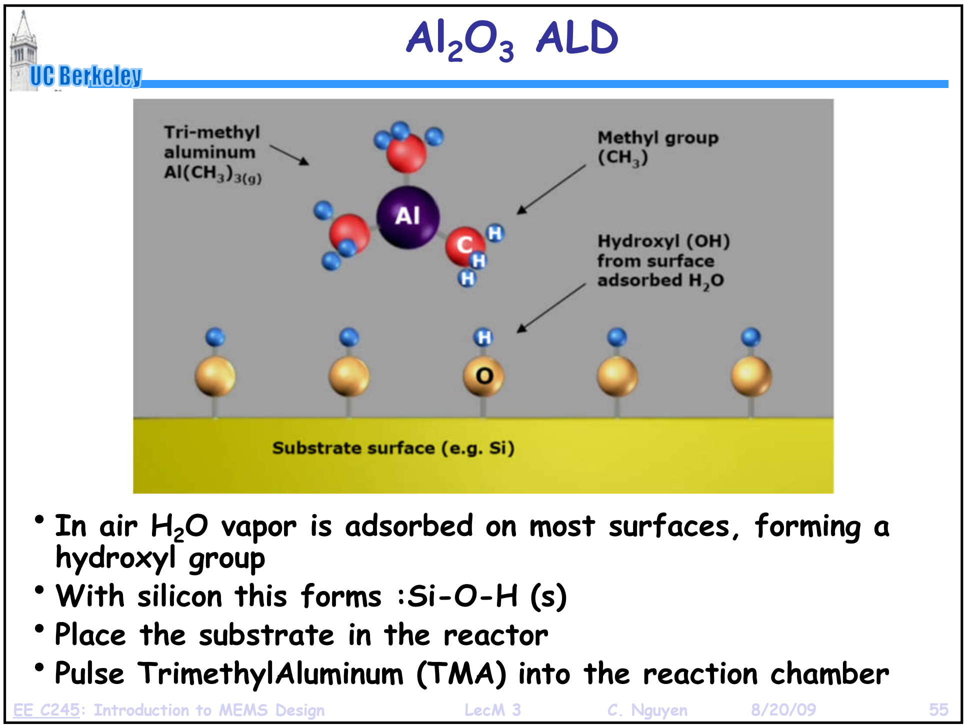


ALD Reactor

200°C to 400°C needed

Must purge completely before the next pulse

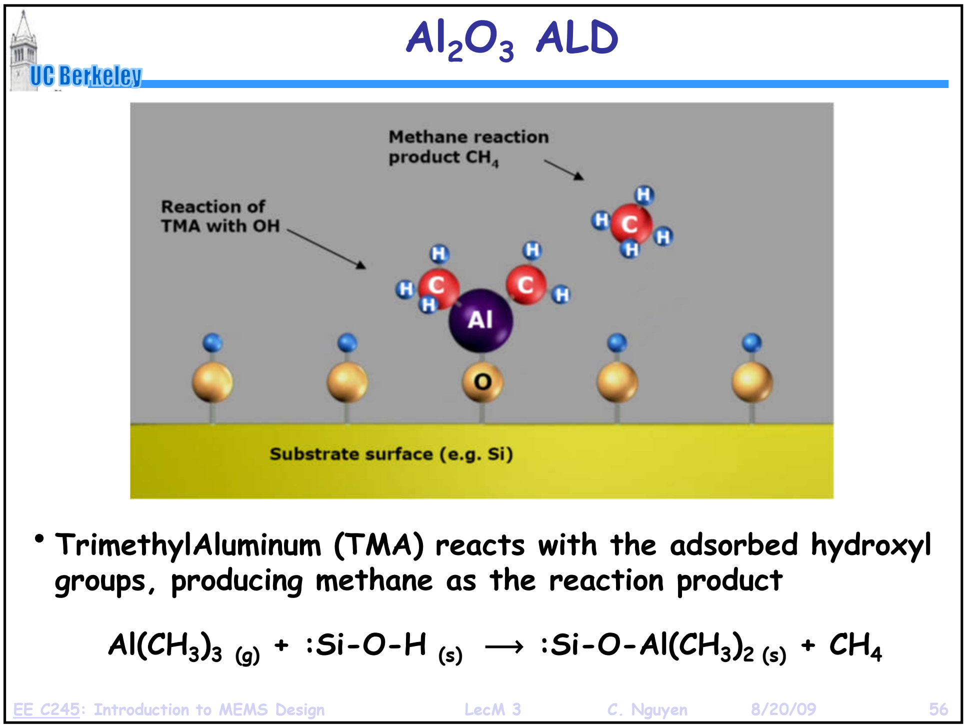
Usually mixed w/ an inert gas to achieve lower effective vapor pressures → slows reaction, but needed to allow rapid pulsing & purging



UC Berkeley

Al_2O_3 ALD

- In air H_2O 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

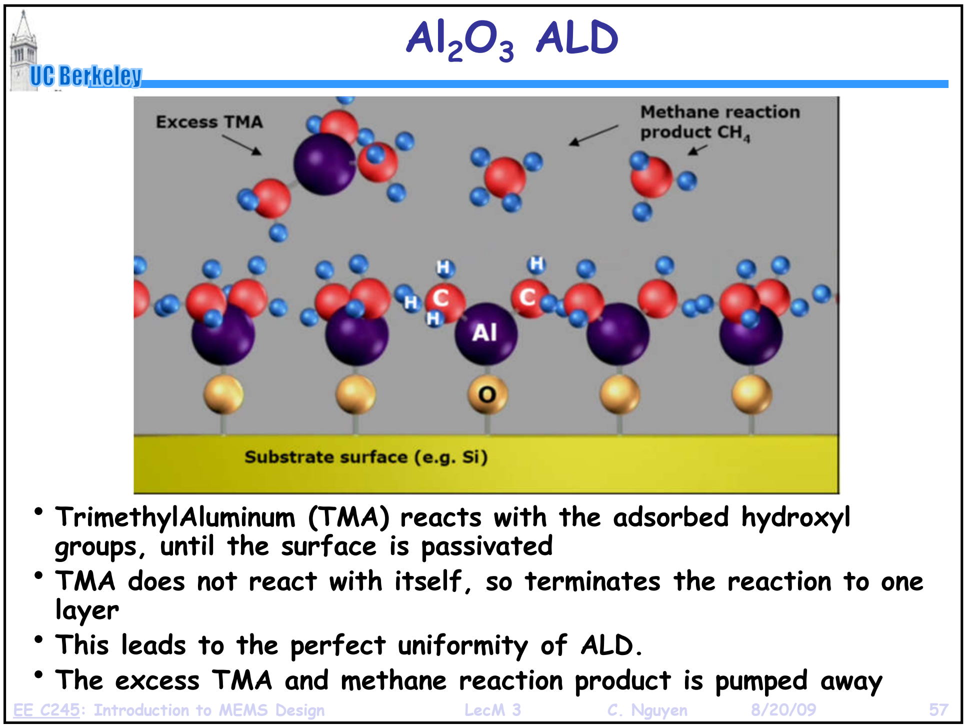


UC Berkeley

Al_2O_3 ALD

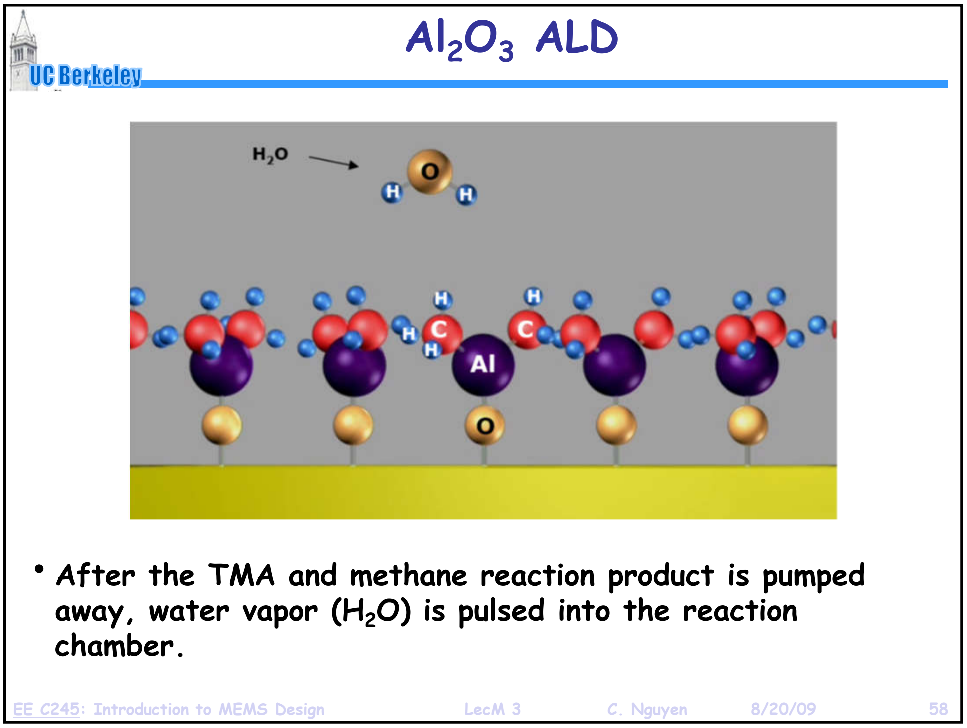
- TrimethylAluminum (TMA) reacts with the adsorbed hydroxyl groups, producing methane as the reaction product

$$Al(CH_3)_{3\ (g)} + :Si\text{-}O\text{-}H_{\ (s)} \longrightarrow :Si\text{-}O\text{-}Al(CH_3)_{2\ (s)} + CH_4$$



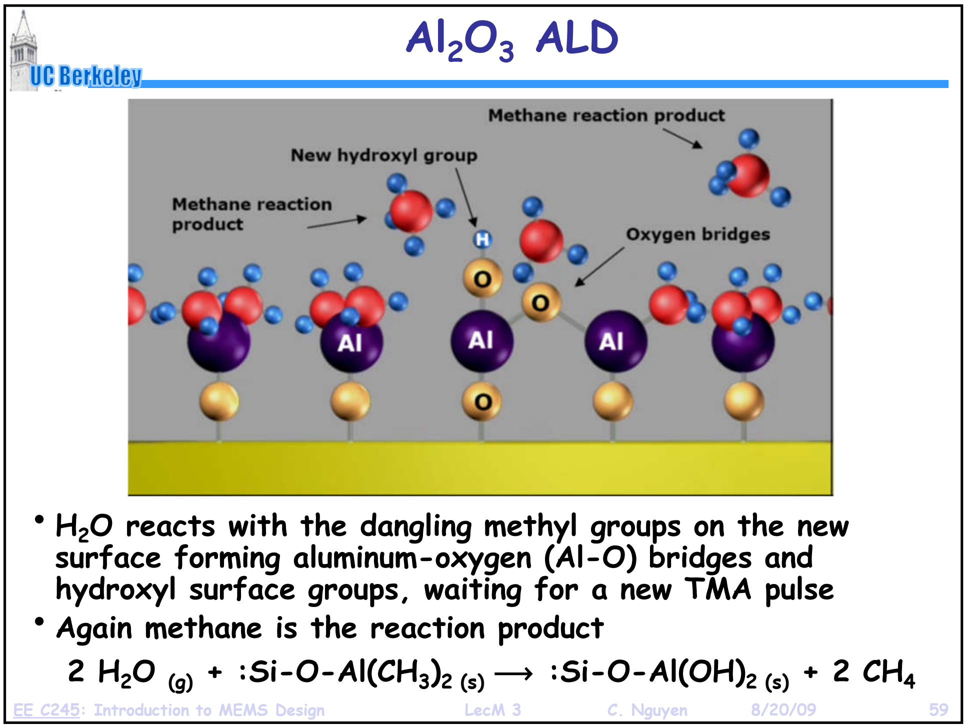
Al_2O_3 ALD

- 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



Al_2O_3 ALD

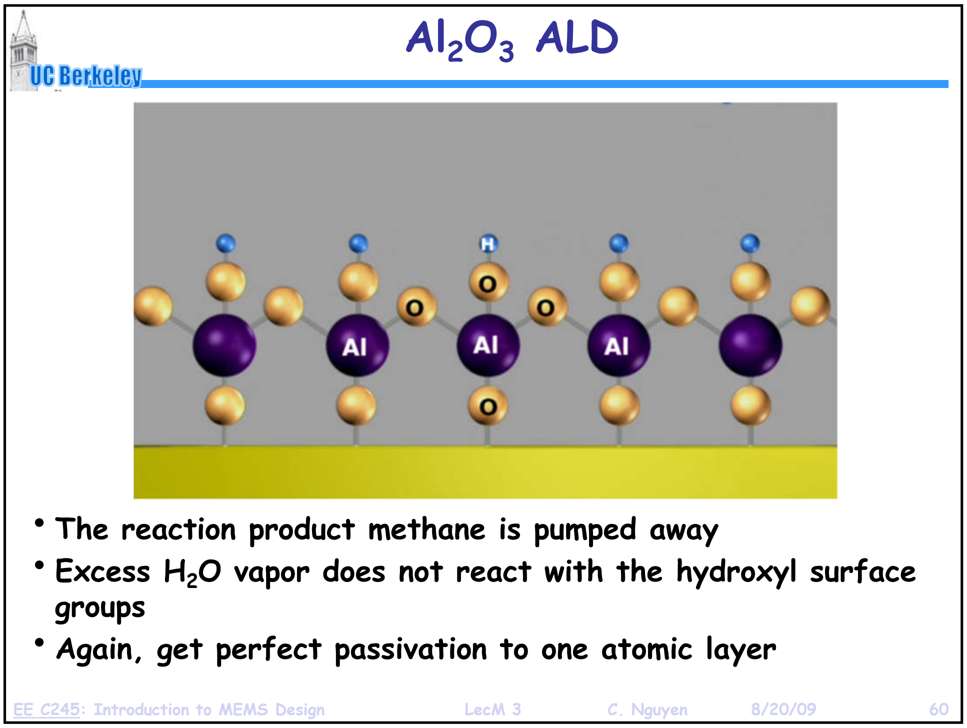
- After the TMA and methane reaction product is pumped away, water vapor (H_2O) is pulsed into the reaction chamber.



Al_2O_3 ALD

- H_2O 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

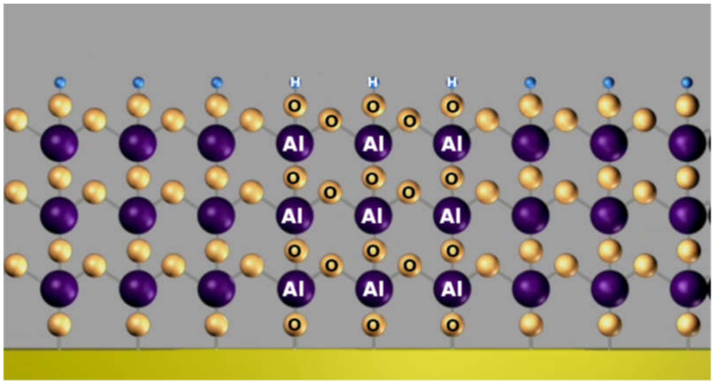
$$2\ H_2O_{(g)} + :Si\text{-}O\text{-}Al(CH_3)_{2\ (s)} \longrightarrow :Si\text{-}O\text{-}Al(OH)_{2\ (s)} + 2\ CH_4$$



Al_2O_3 ALD

- The reaction product methane is pumped away
- Excess H_2O vapor does not react with the hydroxyl surface groups
- Again, get perfect passivation to one atomic layer

Al_2O_3 ALD



- One TMA and one H_2O 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

$$Al(CH_3)_3\,_{(g)} + :Si\text{-}O\text{-}H\,_{(s)} \longrightarrow :Si\text{-}O\text{-}Al(CH_3)_2\,_{(s)} + CH_4$$

$$2\ H_2O\,_{(g)} + :Si\text{-}O\text{-}Al(CH_3)_2\,_{(s)} \longrightarrow :Si\text{-}O\text{-}Al(OH)_2\,_{(s)} + 2\ CH_4$$

ALD Capability

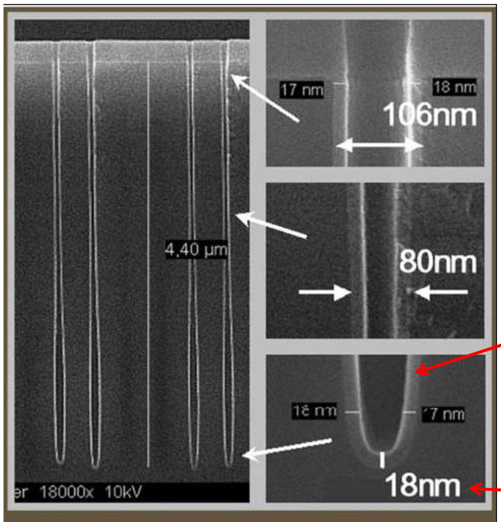
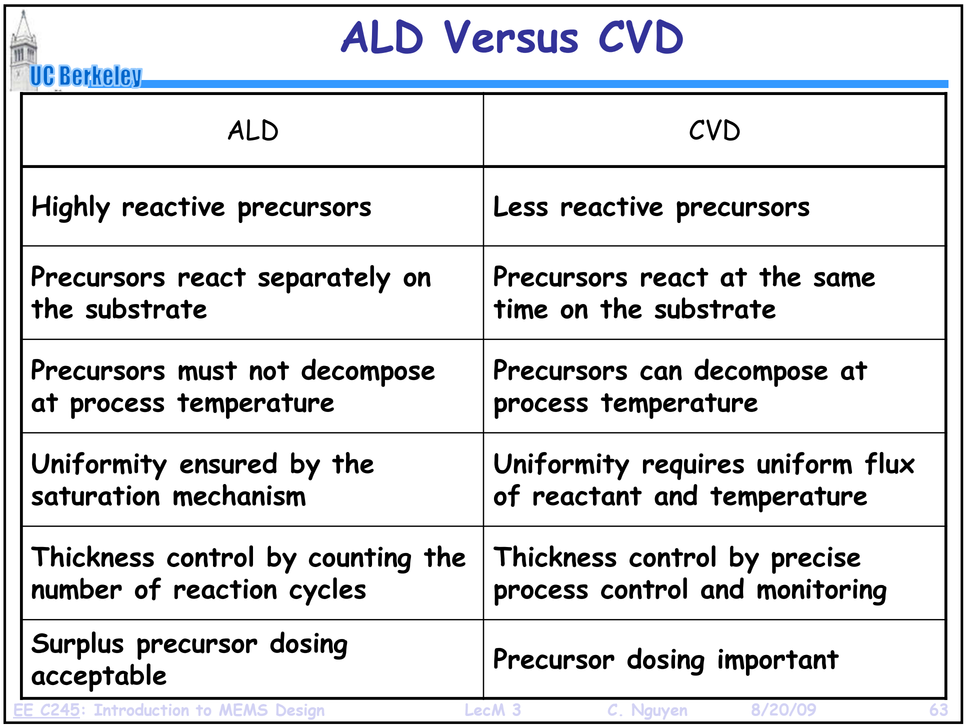


Figure 3. ALD features superb step coverage performance. The SEM images show close to 100% conformality for an 18nm thick Al_2O_3 film which was deposited by ALD into high aspect ratio trenches with a minimum lateral dimension of 80nm and a final aspect ratio of ~ 60.

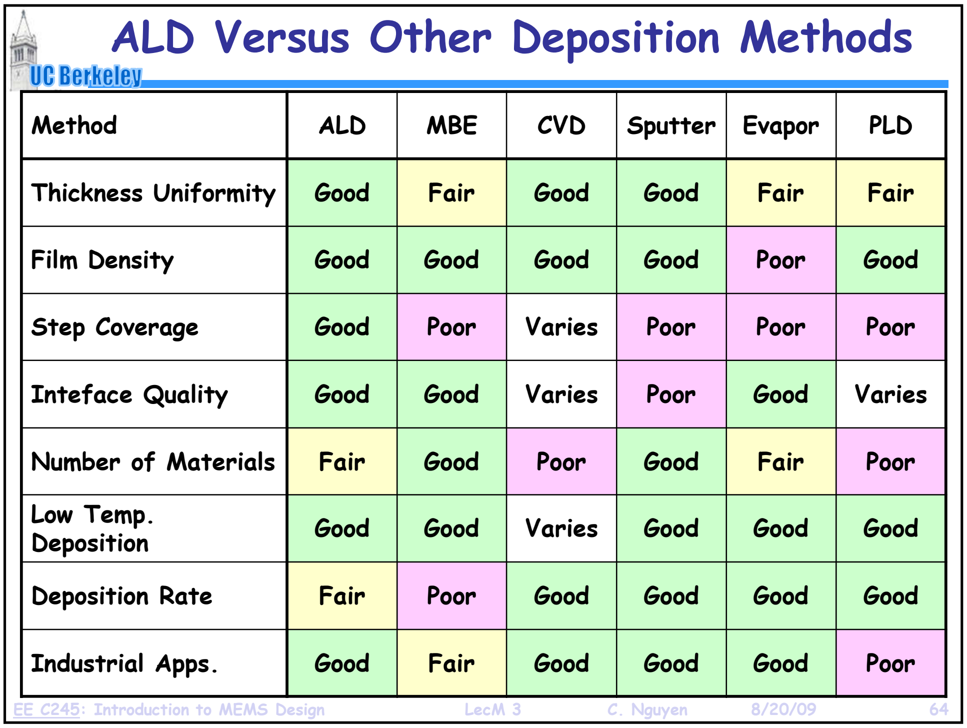
Excellent conformality, even at the bottom of the trench! (aspect ratio ~60:1)

Al_2O_3



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



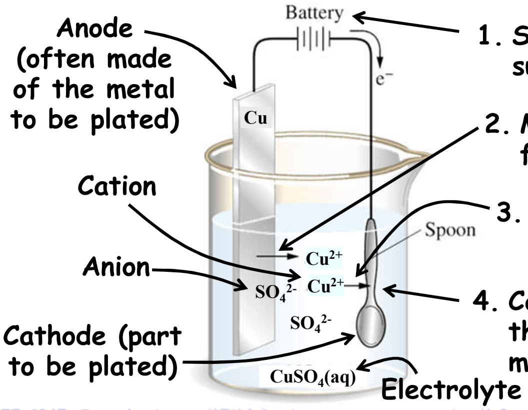
ALD Versus Other Deposition Methods

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
Inteface 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

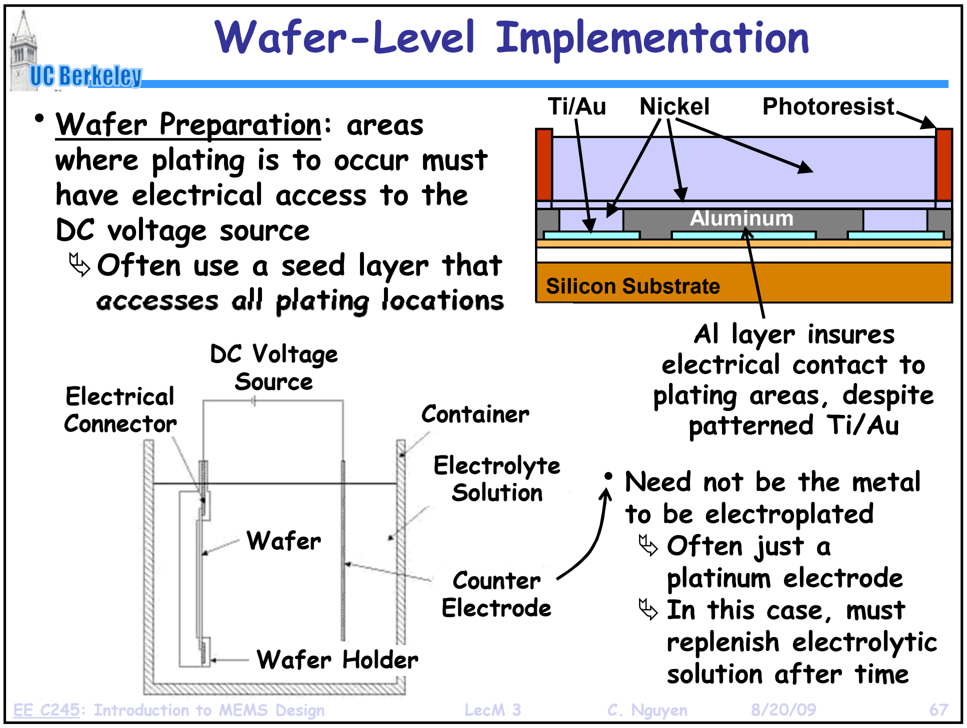
Electroplating

Metal Electroplating

- **Electroplating**: the process using electrical current to coat an electrically conductive object with a thin layer of metal
  - ↳ Useful when very thick (>1μm) 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