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EE C245 - ME C218 Introduction to MEMS Design Fall 2011

Prof. Clark T.-C. Nguyen

Dept. of Electrical Engineering & Computer Sciences
University of California at Berkeley
Berkeley, CA 94720

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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Polysilicon CVD


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


 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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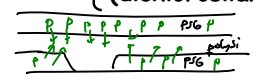
- Phosphosilicate glass can be reflow
 - 6-8 wt. % allows reflow @ 1000-1100°C
 - Very useful to achieve smoother topography
 - Lower concentration → won't reflow
 - Higher concentration → corrodes Al if moisture is present
 - 5-15% P can be used as a diffusion source to dope Si
- Before metallization:**
 - 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.)

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

(Tetraethylorthosilicate) (TEOS) (excellent uniformity & conformal step coverage)

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Silicon Nitride CVD

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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:

Silane reaction: $3\text{SiH}_4 + 4\text{NH}_3 \xrightarrow[700-900^\circ\text{C}]{\text{(Atm. Press.)}} \text{Si}_3\text{N}_4 + 12\text{H}_2$

Dichlorosilane reaction:

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

↖ 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% 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:

Nitrogen discharge

$$\text{SiH}_4 + \text{N}_2 \xrightarrow{\quad\quad\quad} 2\text{SiNH} + 3\text{H}_2$$

or

$$\text{SiH}_4 + \text{NH}_3 \xrightarrow[\text{Ar plasma}]{\quad\quad\quad} \text{SiNH} + 3\text{H}_3$$

}

PECVD films:

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

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Metal CVD

CVD Metal Deposition:

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

$$WF_6 \rightarrow W + 3F_2$$

or via reaction with H_2 :

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

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

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

where $M = Mo, Ta, \text{ or } Ti$

(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.)

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

(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.

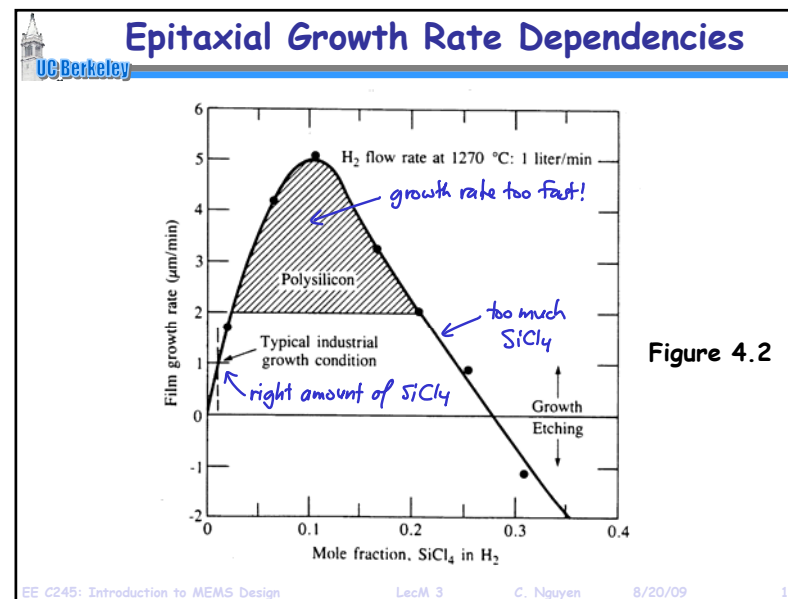
$$SiCl_4 \text{ (gas)} + Si \text{ (solid)} \leftrightarrow 2SiCl_2 \text{ (gas)}$$

↳ 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.)

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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:

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

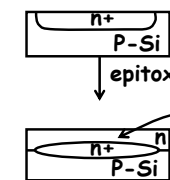
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Doping of Epitaxial Layers

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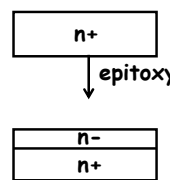
- Use "autodoping" → when growing own heavily-doped substrates
 - Impurity evaporates from wafer (or liberated by Cl etching of surface during dep.)
 - Incorporates into gas stream
 - Impurities dope new layer
 - Examples of autodoping:

Bipolar Processing:



Buried collector to reduce collection R

MOS:



Dopant gradient helps to prevent latch up and punch through

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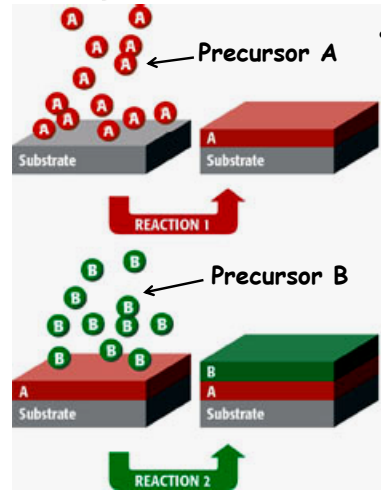
Atomic Layer Deposition (ALD)

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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)

Remarks:

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

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

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

Advantages of ALD

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

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

The graph plots growth cycle against temperature. A dashed horizontal line represents the monolayer thickness. The region where the growth cycle is above the monolayer line is labeled 'Condensation'. The region where the growth cycle is exactly at the monolayer line is labeled 'ALD Window'. The region where the growth cycle is below the monolayer line is labeled 'Decomposition' and 'Re-evaporation'. A region where the growth cycle is below the monolayer line but above zero is labeled 'Incomplete Reaction'.

ALD Reactor

200°C to 400°C needed

Must purge completely before the next pulse

The diagram shows a reactor chamber with a wafer. Two precursor reservoirs (Precursor 1 and Precursor 2) are connected to the chamber via high-speed valves and temperature-controlled baths. Precursor 1 is pulsed into the chamber, followed by a purge pulse (Vapor pulse 1) and a water pulse. Then Precursor 2 is pulsed, followed by another purge pulse (Vapor pulse 2) and a water pulse. The chamber is heated by heaters and has vacuum pumping out.

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

Al₂O₃ ALD

The diagram shows a substrate surface (e.g., Si) with adsorbed hydroxyl groups (OH) from surface-adsorbed H₂O. A Tri-methyl aluminum (TMA) molecule, Al(CH₃)₃, is shown reacting with the hydroxyl group to form a methyl group (CH₃) on the surface and a hydroxyl group on the aluminum atom.

- 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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Reaction of TMA with OH

Methane reaction product CH₄

Substrate surface (e.g. Si)

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

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

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UC Berkeley **Al₂O₃ ALD**

Excess TMA

Methane reaction product CH₄

Substrate surface (e.g. Si)

- 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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UC Berkeley **Al₂O₃ ALD**

H₂O

New hydroxyl group

Oxygen bridges

Methane reaction product

Substrate surface (e.g. Si)

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

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UC Berkeley **Al₂O₃ ALD**

Methane reaction product

New hydroxyl group

Oxygen bridges

Methane reaction product

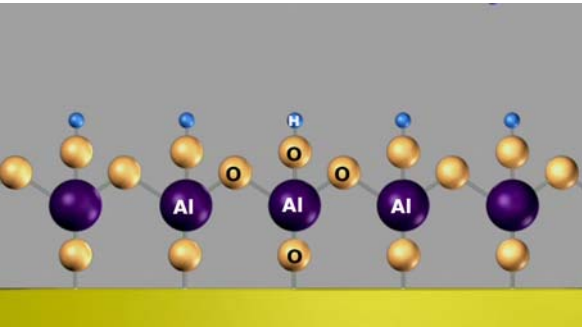
Substrate surface (e.g. Si)

- 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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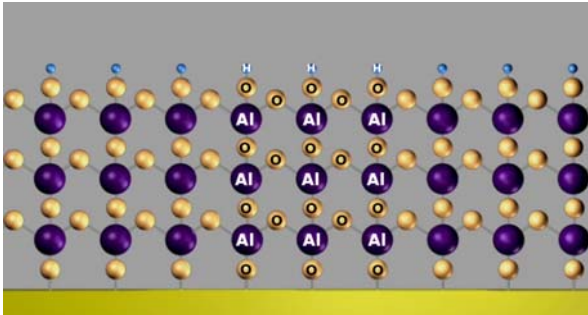
Al₂O₃ ALD



- The 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



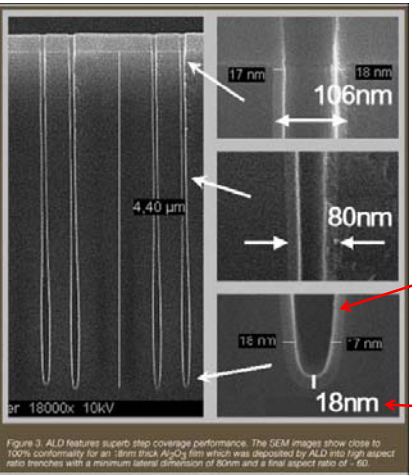
- One TMA and one H₂O vapor pulse form one cycle
- Here, three cycles are shown, with approximately 1 Å per cycle
- Each cycle including pulsing and pumping takes, e.g., 3 sec

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

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

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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

- Switch on external supply of direct current
- Metal at anode is oxidized to form cations with a (+) charge
- Cations are attracted to the (-) charge on the cathode
- 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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