

### 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  $\text{SiCl}_4$ ,  $\text{SiH}_4$ ,  $\text{SiH}_2\text{Cl}_2$  for vapor phase epitaxy.

$\text{SiCl}_4$ : Silicon tetrachloride  
 $\text{SiH}_4$ : silane  
 $\text{SiH}_2\text{Cl}_2$ : dichlorosilane

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### Epitaxy (cont.)

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

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

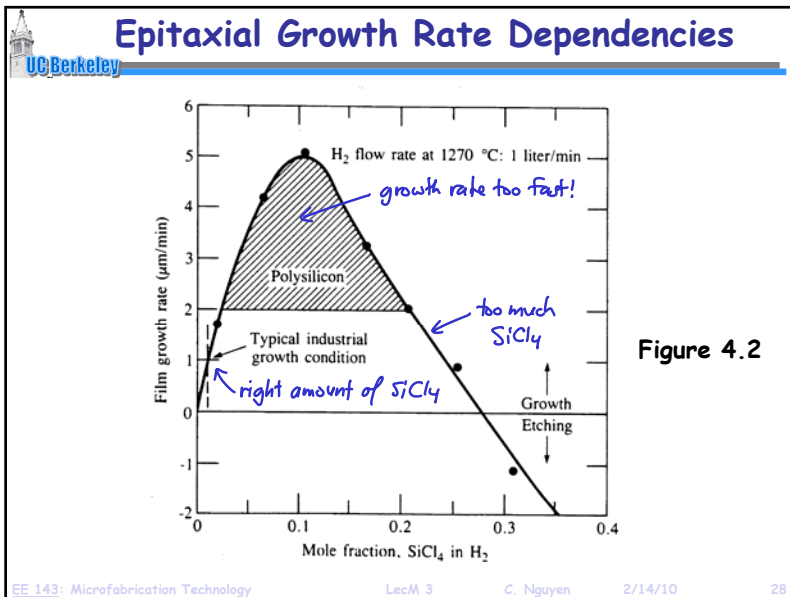
Also get a competing reaction.

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

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

Important that the right conc. of  $\text{SiCl}_4$  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  $\rightarrow$  causes silica formation

**Doping of Epitaxial Layers:**

- Just add impurities during growth: Arsenic, diborane, Phosphine
  - Control resistivity by varying partial pressure of dopant species
    - Arsenic, Phosphine  $\rightarrow$  slow down the growth rate
    - Diborane  $\rightarrow$  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

*low conc. as you go up.*

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### Atomic Layer Deposition (ALD)

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### 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

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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

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### 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 monolayer growth against temperature. It shows a 'Condensation' region at low temperatures where growth is high, an 'ALD Window' in the middle where growth is constant and limited to one monolayer, and a 'Decomposition' region at high temperatures where growth drops to zero. Labels include 'growth cycle', 'monolayer', 'Incomplete Reaction', and 'Re-evaporation'.

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### ALD Reactor

The schematic shows a reactor chamber with a substrate. Two precursor reservoirs (Precursor 1 and Precursor 2) are connected via high-speed valves to the chamber. Precursor 1 is pulsed into the chamber, followed by a purge with water. Precursor 2 is then pulsed, followed by another water purge. Heaters are located above the substrate. The chamber is connected to a vacuum pumping out system.

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 adsorbed hydroxyl groups (OH). A Tri-methyl aluminum (TMA) molecule, Al(CH<sub>3</sub>)<sub>3(g)</sub>, is shown reacting with the hydroxyl group. The reaction produces a methyl group (CH<sub>3</sub>) on the surface and a hydroxyl group on the aluminum atom.

- 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 a hydroxyl group on a substrate surface. The reaction produces a methyl group on the surface and methane (CH<sub>4</sub>) as the reaction product.

- 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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UC Berkeley **Al<sub>2</sub>O<sub>3</sub> ALD**

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

- 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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UC Berkeley **Al<sub>2</sub>O<sub>3</sub> ALD**

- 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

$$2 \text{H}_2\text{O}_{(g)} + \text{:Si-O-Al(CH}_3)_2_{(s)} \rightleftharpoons \text{:Si-O-Al(OH)}_2_{(s)} + 2 \text{CH}_4$$

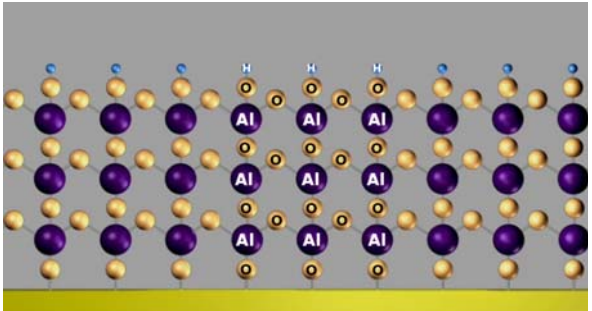
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UC Berkeley **Al<sub>2</sub>O<sub>3</sub> ALD**

- 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



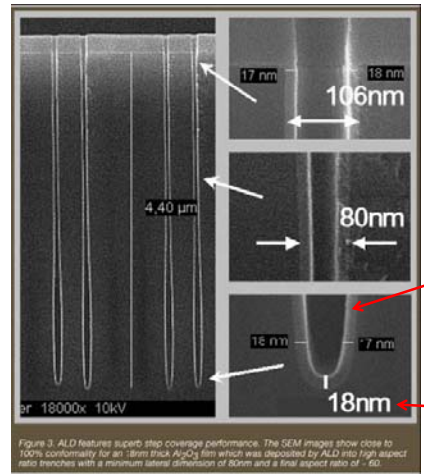
- One TMA and one H<sub>2</sub>O vapor pulse form one cycle
- Here, three cycles are shown, with approximately 1 Å per cycle
- Each cycle including pulsing and pumping takes, e.g., 3 sec

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

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

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### ALD Capability



Excellent conformity, 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% conformity 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 diffusion 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

All Al 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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