

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 ($<500^{\circ}\text{C}$) to prevent hillocks from growing on Al surfaces
 - Similar issues for copper (Cu) metallization
- Low temperature reactions:

LPCVD
LTO
Reactions

$\text{SiH}_4 + \text{O}_2 \xrightarrow{300-500^{\circ}\text{C}} \text{SiO}_2 + 2\text{H}_2$
 (silane)

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

$\text{SiO}_2 + 2\text{H}_2$
 $2\text{P}_2\text{O}_5 + 6\text{H}_2$

Phosphosilicate glass (PSG)

~450°C ← too low for conformal film

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

Silicon Oxide CVD (cont.)

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


HTO { $\text{SiCl}_2\text{H}_2 + 2\text{N}_2\text{O} \xrightarrow{\sim 900^\circ\text{C}} \text{SiO}_2 + 2\text{N}_2 + 2\text{HCl}$

(dichlorosilane) (Nitrous oxide) (nice conformal step coverage)

MEMS: or ...

EE 143: Microfabrication Technology
LecM 3
C. Nguyen
2/14/10
21

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)

EE 143: Microfabrication Technology LecM 3 C. Nguyen 2/14/10 22

Silicon Nitride CVD

UC Berkeley

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

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

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

Problem: Clobbers your pumps! Expensive to maintain!

EE 143: Microfabrication Technology LecM 3 C. Nguyen 2/14/10 23

Silicon Nitride CVD (cont.)

Comments on LPCVD nitride films:

- Hydrogen rich: ~8% H₂ *for stoichiometric nitride: Si₃N₄*
- High internal tensile stresses: films >1000Å crack and peel due to excessive stress
- Can get 2μm films with Si-rich nitride *100nm*
- LPCVD gives high resistivity (10¹⁶ Ω-cm) and dielectric strength (10 MV/cm)

PECVD Nitride:

Nitrogen discharge

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

or

Ar plasma

$$\text{SiH}_4 + \text{NH}_3 \longrightarrow \text{SiNH} + 3\text{H}_2$$

PECVD films:

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

EE 143: Microfabrication Technology LecM 3 C. Nguyen 2/14/10 24

Metal CVD

CVD Metal Deposition:

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

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

or via reaction with H₂:

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

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

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

where M = Mo, Ta, or Ti

(Even Al can be CVD'ed with tri-isobutyl Al ... but other methods are better.)
(Cu is normally electroplated)

EE 143: Microfabrication Technology LecM 3 C. Nguyen 2/14/10 25

Epitaxy

Epitaxy: *Normal CVD* *polycrystalline* } *Epitaxy* *Si*

- 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 SiCl₄, SiH₄, SiH₂Cl₂ for vapor phase epitaxy.

SiCl₄: Silicon tetrachloride
SiH₄: silane
SiH₂Cl₂: dichlorosilane

EE 143: Microfabrication Technology LecM 3 C. Nguyen 2/14/10 26

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.

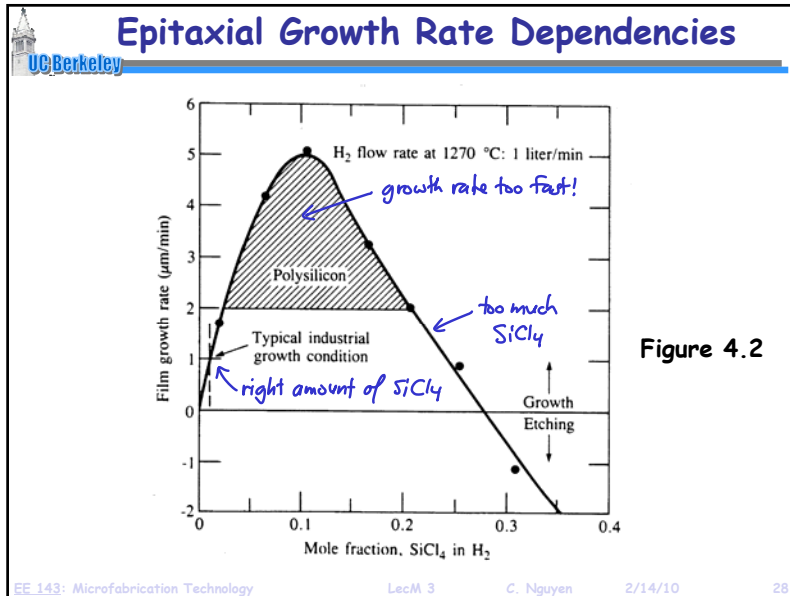
$$\text{SiCl}_4 (\text{gas}) + \text{Si} (\text{solid}) \longleftrightarrow 2\text{SiCl}_2 (\text{gas})$$

- Too much SiCl₄ → 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 SiCl₄ is used!

EE 143: Microfabrication Technology LecM 3 C. Nguyen 2/14/10 27



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:

- 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

EE 143: Microfabrication Technology LecM 3 C. Nguyen 2/14/10 29

Doping of Epitaxial Layers

- 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:

EE 143: Microfabrication Technology LecM 3 C. Nguyen 2/14/10 30

Atomic Layer Deposition (ALD)

EE 143: Microfabrication Technology LecM 3 C. Nguyen 2/14/10 31

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

EE 143: Microfabrication Technology LecM 3 C. Nguyen 2/14/10 32

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

EE 143: Microfabrication Technology LecM 3 C. Nguyen 2/14/10 33

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:

EE 143: Microfabrication Technology LecM 3 C. Nguyen 2/14/10 34

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 \rightarrow slows reaction, but needed to allow rapid pulsing & purging

EE 143: Microfabrication Technology LecM 3 C. Nguyen 2/14/10 35

Al₂O₃ ALD

Tri-methyl aluminum $\text{Al}(\text{CH}_3)_3(g)$

Methyl group (CH_3)

Hydroxyl (OH) from surface adsorbed H_2O

Substrate surface (e.g. Si)

- In air H_2O vapor is adsorbed on most surfaces, forming a hydroxyl group
- With silicon this forms $:\text{Si}-\text{O}-\text{H}(s)$
- Place the substrate in the reactor
- Pulse TrimethylAluminum (TMA) into the reaction chamber

EE 143: Microfabrication Technology LecM 3 C. Nguyen 2/14/10 36

Al₂O₃ ALD

Methane reaction product CH_4

Reaction of TMA with OH

Substrate surface (e.g. Si)

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

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

EE 143: Microfabrication Technology LecM 3 C. Nguyen 2/14/10 37

Al₂O₃ ALD

Excess TMA

Methane reaction product CH_4

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

EE 143: Microfabrication Technology LecM 3 C. Nguyen 2/14/10 38

Al₂O₃ ALD

H_2O

Substrate surface (e.g. Si)

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

EE 143: Microfabrication Technology LecM 3 C. Nguyen 2/14/10 39

Al₂O₃ ALD

- 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

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

EE 143: Microfabrication Technology LecM 3 C. Nguyen 2/14/10 40

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

EE 143: Microfabrication Technology LecM 3 C. Nguyen 2/14/10 41

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

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

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

EE 143: Microfabrication Technology LecM 3 C. Nguyen 2/14/10 42

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 18 nm thick Al₂O₃ film which was deposited by ALD into high aspect ratio trenches with a minimum lateral dimension of 80 nm and a final aspect ratio of ~60.

EE 143: Microfabrication Technology LecM 3 C. Nguyen 2/14/10 43

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
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

Electroplating

Metal Electroplating

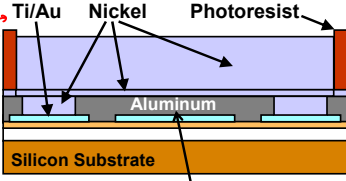
- Electroplating:** the process using electrical current to coat an electrically conductive object with a thin layer of metal
 - Useful when very thick ($>1\mu\text{m}$) metal films are needed
 - Evaporation and sputtering generally suffer from excessive stress when films get too thick \rightarrow get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

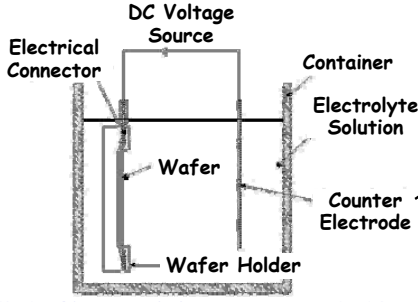
Wafer-Level Implementation

UC Berkeley

- **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

EE 143: Microfabrication Technology LecM 3 C. Nguyen 2/14/10 48