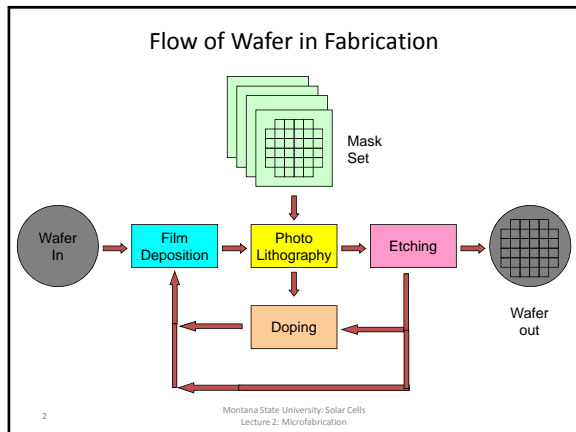


### EE580 – Solar Cells Todd J. Kaiser

- Lecture 02 Microfabrication
  - A combination of Applied Chemistry, Physics and Optics
- Thermal Processes
  - Diffusion & Oxidation
- Photolithography
- Deposition
- Etching

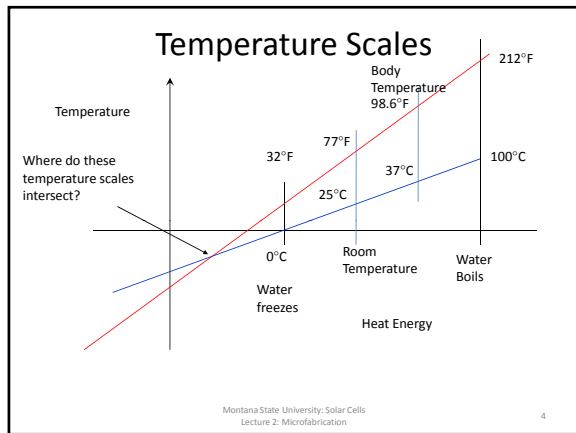
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### Questions

- **What is heat?**
- Heat is the internal energy of a solid which is stored as atom vibration.
- **What is heat flow?**
- Heat flow represents the transfer from hot to cold of energy by the random motion and collisions of atoms and molecules
- Heat is removed by:
  - Conduction through solids
  - Convection through fluids and gases
  - Radiation through no medium (IR)
- **What is temperature?**
- Temperature is a measure of the mean kinetic energy of the molecules.

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### Temperature Conversions

$$F = 32 \Leftrightarrow C = 0 \quad F = 212 \Leftrightarrow C = 100$$

$$F = \frac{212-32}{100-0}C + 32 = \frac{180}{100}C + 32 = \frac{9}{5}C + 32$$

if  $F = C \Rightarrow F = \frac{9}{5}F + 32$

$$-\frac{4}{5}F = 32 \Rightarrow F = \left(-\frac{5}{4} \times 32\right) = -40^\circ F = -40^\circ C$$

$$^\circ K = 273 + ^\circ C$$

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### Thermally Activated Processes

- Thermal energy required to initiate process.
- Diffusion
  - Interstitial impurity atoms move in lattice

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### Thermally Activated Process

Energy below the activation energy

Energy above the activation energy

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### Diffusion

- Movement of particles from high concentration to low concentration
- Mass transport within solids by step-wise atomic motion
- Thermal energy drives reaction

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### Vacancy Diffusion

Vacancy

- Requires vacancies (defects)
- Rate a function of the number of defects present

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### Interstitial Diffusion

- More rapid than vacancy diffusion
- More empty interstitial positions than vacancies

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### Diffusion

Process where particles tend to spread out or redistribute due to random thermal motion from high concentration to low concentration

Ex: spill a beer and eventually the whole room smells like a brewery  
Or perfume

1-D system particles have an equally chance of jumping left or right due to thermal energy, if hit a wall bounce back to original bin

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### Diffusion – (doping Si)

- Activation energy-energy required to get over potential barrier (change location)

$$D = D_0 \exp\left(-\frac{E_A}{kT}\right)$$

Arrhenius Rate Equation

- How far does the impurity move- root mean displacement

$$L = \sqrt{2[D(T)t]_{total}}$$

$$L = \sqrt{2\left(\sum_i D_i t_i\right)}$$

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### Diffusion Reactions

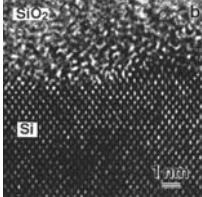
$$2B_2O_3 + 3Si \leftrightarrow 4B + 3SiO_2$$

$$2P_2O_5 + 5Si \leftrightarrow 4P + 5SiO_2$$

Dopant Sources	Substrate Silicon	Doping Elements	Silicon Dioxide
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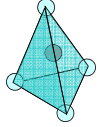
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### Silicon Oxide



SiO<sub>2</sub>

Si

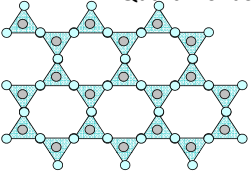


(SiO<sub>4</sub>)<sup>4-</sup>  
tetrahedron

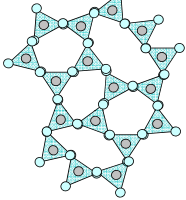
Silicon and four closest oxygen atoms

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### Quartz vs fused silica



Crystalline Quartz

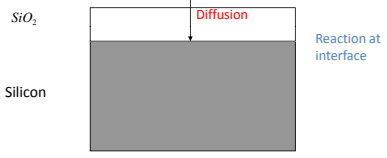


Amorphous fused silica

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### Thermal Oxidation of Silicon

Ambient	Dry O <sub>2</sub>	Wet H <sub>2</sub> O
$Si + O_2 \rightarrow SiO_2$	$Si + 2H_2O \rightarrow SiO_2 + 2H_2$	

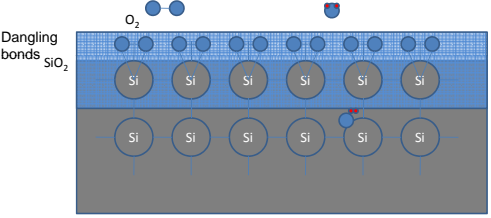


Which method gives the better quality insulator Wet or Dry oxidation? Why?  
Which method is faster? Why?

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### Oxidation of Silicon

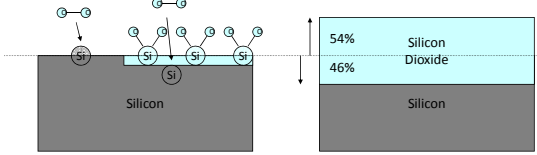
Dry oxidation slower (larger molecules) but better quality of oxide.  
Wet oxidation faster but quality suffers due to the diffusion of the hydrogen gas out of the film. This creates paths that electrons can follow.



Dangling bonds SiO<sub>2</sub>

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### Silicon Consumed in Oxidation



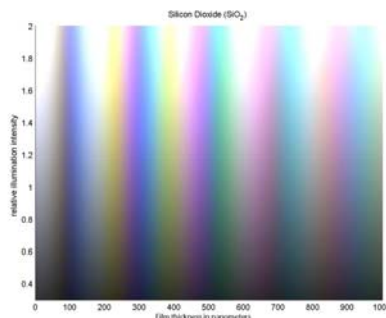
Oxide grows at the silicon-oxide interface.  
Oxygen or water vapor must diffuse through the oxide to reach the interface. This limits the practical thickness that can be grown.  
The resulting oxide expands out of the surface, which creates high compressive stress.

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### Thermal Oxidation of Silicon

- Silicon oxidizes on exposure to oxygen
  - “Dry”:  $Si + O_2 \rightarrow SiO_2$
  - “Wet”:  $Si + 2H_2O \rightarrow SiO_2 + 2H_2$
- Room temperature in air creates “Native Oxide”
  - Very Thin - ~1nm – poor insulator, but can impede surface processing of Si
- Dry Oxide: 900-1200°C in  $O_2$ 
  - Thin 0.05-0.5µm : Excellent insulator: gate oxides
- Wet Oxide: 900-1200°C in  $H_2O$ 
  - Thick <2.5µm : Good Insulator: field oxides, Masking

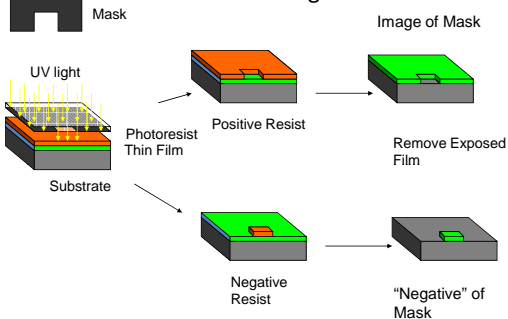
### Color Chart



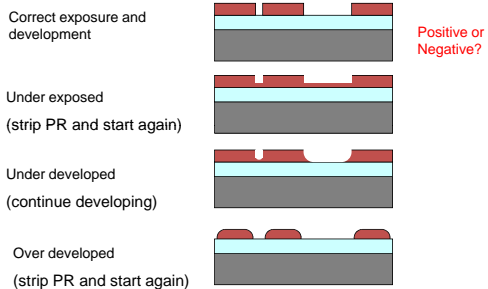
### Photolithography

- Lithography is the basic technique to define and transfer patterns in most microfabrication procedures
- Photolithography uses UV light through a mask onto a photosensitive organic (photoresist, PR)
- Positive resist → exposed resist is removed in developer → “What shows goes” (image of mask)
  - Shipley 1813
- Negative resist → UV light cross-links polymer and developer rinses away non-cross-linked chains → exposed remains (negative of mask)
- PR protects region for the next process step

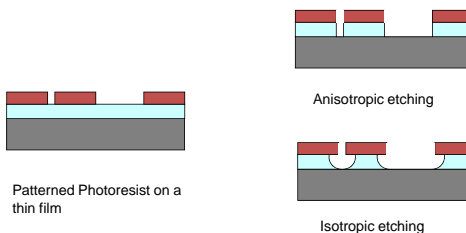
### Positive Resist vs Negative Resist



### Exposure/Developing



### Thin Film Etching



1) Deposit Film

2) Apply Photoresist

3) Expose Photoresist

4) Develop Photoresist

5) Transfer Pattern

Thin Film Substrate

Photoresist

UV Light

Mask

Positive or Negative?

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### Apply Photoresist

- Open top cover to access vacuum chuck.
- Make sure 4" chuck is in place
- Place wafer on vacuum chuck. Use the centering tool to make sure the wafer is in the center. It is important to make sure the flats aren't used in the centering process.
- Close cover.
- Press **RUN** then **9** then **Start** to start program 9. Record rate and time
- Watch to make sure the wafer doesn't wobble when it does the test spin.
- If the wafer doesn't wobble then press **Start** again.
- Watch the timer on the spinner when it dispenses the PR you may have to hold down the plunger.
- Once it is dispensed close the door to the fume hood.

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### Prebake

- Press **Option, Start, Run, 9**
- Place wafer on hot plate and push to the pins on the hot plate.
- Wait for the vacuum on the hot plate to initiate the process
- Watch counter
- Take the wafer off as soon as the counter reaches zero.

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### ABM Contact Aligner

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### Alignment position

- Groups of alignment marks should be placed near the perimeter of the mask sets

Microscope objectives

- Makes rotational alignment easier
- Alignment is iterative process x-y then theta, x-y then theta...

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### Exposure

- Turn on vacuum pump.
- Put mask on the mask holder and turn on the vacuum. (Insert mask with chrome side down)
- Raise the wafer stage (switch on the right)
- Load wafer onto vacuum chuck. Turn on vacuum chuck. Beware of flat position
- Lower stage.
- Raise wafer until it comes in contact with the mask. You will feel the micrometer knob slip.

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### Aligner Mask Holder

- Lower wafer 100  $\mu\text{m}$
- Calculate the exposure time
- Auto expose. Don't look at the light.
- Remove mask and wafer.
- Leave the machine on.



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### Development

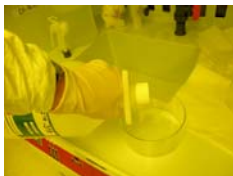
- PR comes with corresponding developer.
- Typically a KOH dissolved in water that reacts with PR to form amines and metallic salts
- Very temperature sensitive chemical reaction, therefore need to monitor or set temperature.
- After development a hard bake is used to further set the PR and drive off absorbed water and solvent.

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### Develop

- MF 319
- Pour developer into crystallization dish
- Time the development
- Record time and developer concentration
- Rinse and inspect
- If PR is not entirely removed in exposed areas, return to developer
- Record additional time

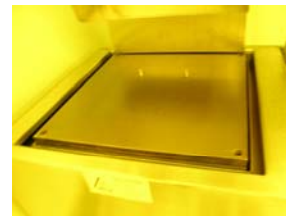


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### Postbake

- If patterns are well defined post bake
- This drives off the remaining solvent
- Record time and temperature



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### Wet Etching Silicon Dioxide

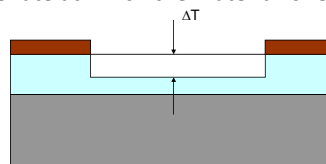
- HF supplied by vendor is 49%
  - Etch rate too fast
- $\text{SiO}_2 + 6\text{HF} \rightarrow \text{H}_2\text{SiF}_6 + 2\text{H}_2\text{O}$
- Reaction consumes HF  $\rightarrow$  rate will be function of time
- Buffering agent added to maintain HF concentration
  - Ammonium Fluoride:  $\text{NH}_4\text{F}$
- 6:1 Buffered Oxide Etch
  - 6:1  $\rightarrow$   $\text{NH}_4\text{F}:\text{HF}$  (40%:49%)

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### Etch Rate

- The rate at which the material is removed



$$\text{etch rate} = \frac{\Delta T}{\Delta t} = \frac{\text{change in thickness}}{\text{change in time}}$$

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### Etch Oxide (HF solution)

- BOE 6:1
- Etch rate 900nm/min
- Calculate required time for your oxide thickness
- Approx. 5-6 minutes
- Rinse and dry
- It is better to over etch at this step than under etch.
- Record time and concentration used



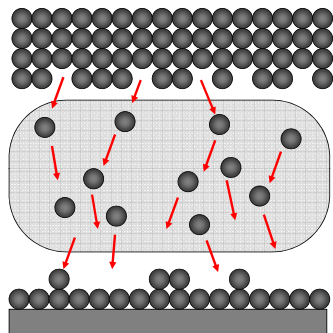
### Solvent Clean

- Acetone-Red
- Isopropyl Alcohol-Blue
- Methanol -Green
- DI water
- Dry with nitrogen gun
- Store wafer in dry box

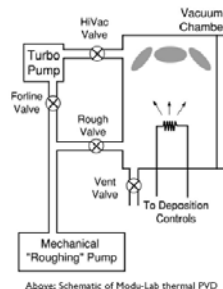


### 3 Basics Steps of Evaporation

- Atoms from a solid are vaporized
- Vaporized atoms are transported through a reduced pressure region
- Atoms condense on a solid surface to form a thin film



### Our Physical Vapor Deposition (PVD)



Above: Schematic of Modu-Lab thermal PVD

### PVD: Loading the Wafers



Upper Left: Aluminum evaporation sample loaded into Filament  
Upper Right: Loading a wafer into Wafer Holder



Upper Left: Close-up of a spring clip  
Upper Right: Fully-loaded Wafer Holder

### PVD: Mounting the Filament



Upper Left: Replacing loaded Filament into screw clamps  
Upper Right: Close-up of ridges on screw clamps



Upper Left: Replacing Filament Shield  
Upper Right: Replacing loaded Wafer Holder

## PVD: Images of the filament



Above: Aluminum sample begins to melt at DFC = 40%



Above: Aluminum sample evaporates at DFC = 60%

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## PVD: Unloading



Upper: Right: Chamber is equalized and door is easily opened

Upper: Left: Unloaded wafer with evaporated aluminum film



Above: Spring clip mark on edge of wafer  
If this mark is not visible, evaporation may not have taken place. This film can be characterized with conductivity measurements or profilometer data

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## Wet Etching Aluminum

- Phosphoric-Acetic-Nitric Acids (PAN etch)
  - 16:1:1:2 →  $\text{H}_3\text{PO}_4:\text{CH}_3\text{COOH}:\text{HNO}_3:\text{H}_2\text{O}$
  - Heated to 35-45°C
  - 350Å/minute
- Nitric oxidizes Al →  $\text{Al}_2\text{O}_3$
- Phosphoric dissolves alumina
- By product hydrogen gas
  - Do under fume hood
  - Gas bubbles can micro-mask

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