# EE 143
# Microfabrication Technology
# Spring 2010

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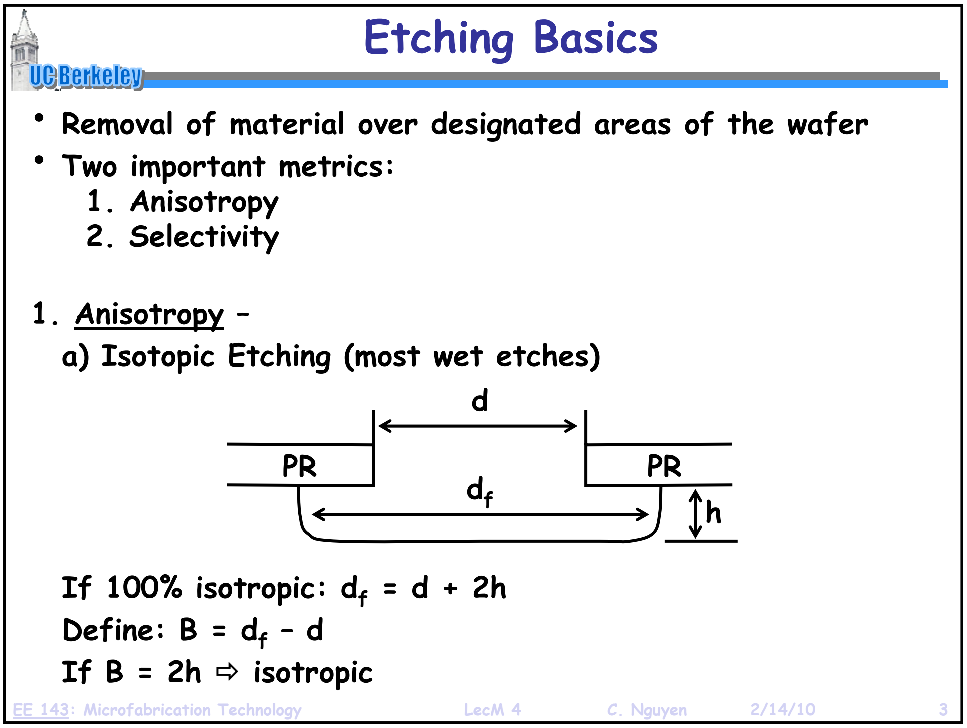
Lecture Module 4: Etching

# Etching



## Etching Basics

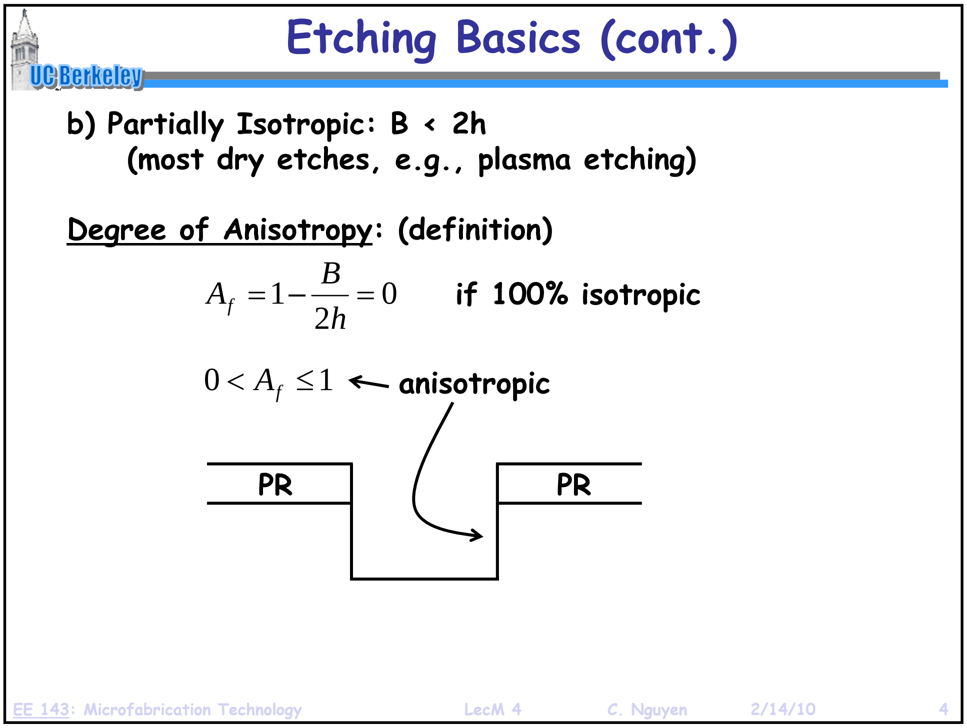
- Removal of material over designated areas of the wafer
- Two important metrics:
  1. Anisotropy
  2. Selectivity

1. Anisotropy –
   a) Isotopic Etching (most wet etches)

If 100% isotropic: $d_f = d + 2h$

Define: $B = d_f - d$

If $B = 2h$ ⇨ isotropic



## Etching Basics (cont.)

b) Partially Isotropic: $B < 2h$
(most dry etches, e.g., plasma etching)

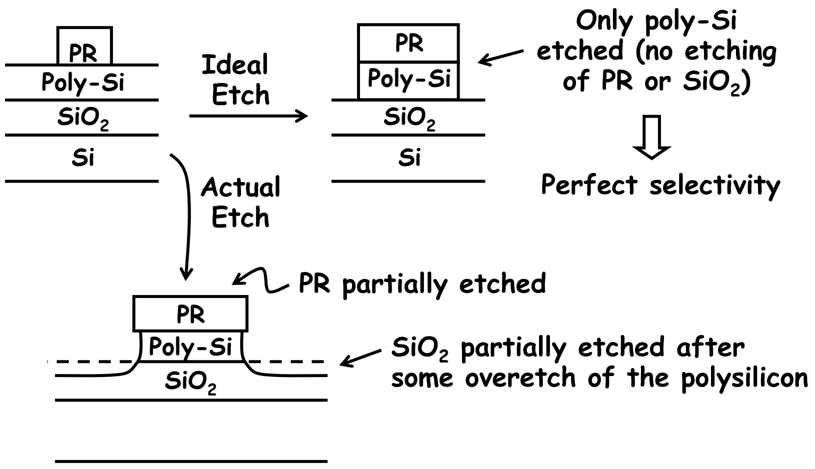
Degree of Anisotropy: (definition)

$$A_f = 1 - \frac{B}{2h} = 0 \quad \text{if 100\% isotropic}$$

$$0 < A_f \leq 1 \leftarrow \text{anisotropic}$$

## Etching Basics (cont.)

2. Selectivity -



Only poly-Si etched (no etching of PR or $SiO_2$)

⇩

Perfect selectivity

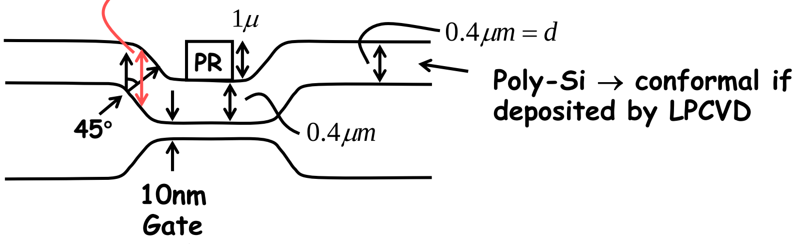
PR partially etched

$SiO_2$ partially etched after some overetch of the polysilicon

## Etching Basics (cont.)

Why overetch?

$\sqrt{2}d = 1.4d = 0.56\mu m$ → Thicker spots due to topography!



Poly-Si → conformal if deposited by LPCVD

Thus, must overetch at least 40%:
40% overetch → (0.4)(0.4) = 0.16 μm poly
= ??? oxide

Depends on the selectivity of poly-Si over the oxide

## Etching Basics (cont.)

Define selectivity of A over B:

$$S_{ab} = \frac{E.R._a}{E.R._b}$$

$E.R._a$ ← Etch rate of A

$E.R._b$ ← Etch rate of B

$S_{ab}$ ← Selectivity of A over B

e.g., wet poly etch ($HNO_3$ + $NH_4$ + $H_2O$)

$$S_{poly/SiO_2} = \frac{15}{1}$$ (very good selectivity)

$S_{poly/PR} =$ Very high (but PR can still peel off after soaking for > 30 min., so beware)

e.g., polysilicon dry etch:

$$S_{poly/SiO_2} = \frac{5-7}{1}$$ ← Regular RIE (but depends on type of etcher)

$$S_{poly/PR} = \frac{4}{1}$$

ECR: 30:1
Bosch: 100:1 (or better)

## Etching Basics (cont.)

If $S_{poly/SiO_2} = \frac{8}{1}$ $\Rightarrow$ 40% overetch removes

$$\frac{0.16}{8} = 20\text{ nm of oxide!}$$

$\Rightarrow$ This will etch all poly over the thin oxide, etch thru the 10nm of oxide, then start etching into the silicon substrate → needless to say, this is bad!

with better selectivity:

e.g., $S_{poly/SiO_2} = \frac{30}{1}$

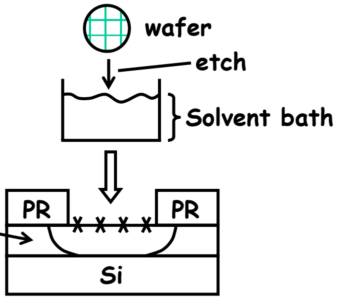
(Can attain with high density Cl plasma ECR etch!)

40% overetch removes $\frac{0.16}{30} = 5.3nm$ (better)

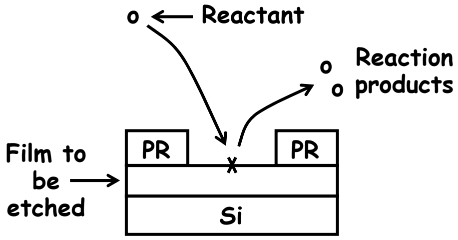
# Wet Etching

# Wet Etching

- **Wet etching**: dip wafer into liquid solution to etch the desired film
  - ↳ Generally isotropic, thus, inadequate for defining features < 3μm-wide



- **General Mechanism** -



1. Diffusion of the reactant to the film surface
2. Reaction: adsorption, reaction, desorption
3. Diffusion of reaction products from the surface

## Wet Etching (cont.)

- There are many processes by which wet etching can occur
  - ↳ Could be as simple as dissolution of the film into the solvent solution
  - ↳ Usually, it involves one or more chemical reactions
    - ☛ Oxidation-reduction (redox) is very common:
      (a) Form layer of oxide
      (b) Dissolve/react away the oxide

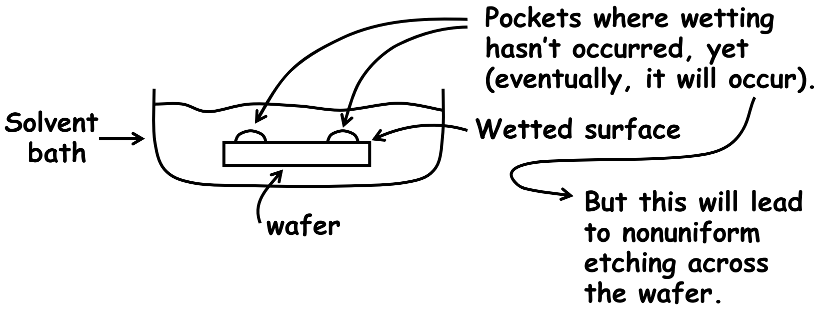
- <u>Advantages</u>:
  1. High throughput process → can etch many wafers in a single bath
  2. Usually fast etch rates (compared to many dry etch processes)
  3. Usually excellent selectivity to the film of interest

## Wet Etching Limitations

1. Isotropic
   - ↳ Limited to <3μm features
   - ↳ But this is also an advantage of wet etching, e.g., if used for undercutting for MEMS
2. Higher cost of etchants & DI water compared w/ dry etch gas expenses (in general, but not true vs. deep etchers)
3. Safety
   - ↳ Chemical handling is a hazard
4. Exhaust fumes and potential for explosion
   - ↳ Need to perform wet etches under hood
5. Resist adhesion problems
   - ↳ Need HMDS (but this isn't so bad)

## Wet Etch Limitations (cont.)

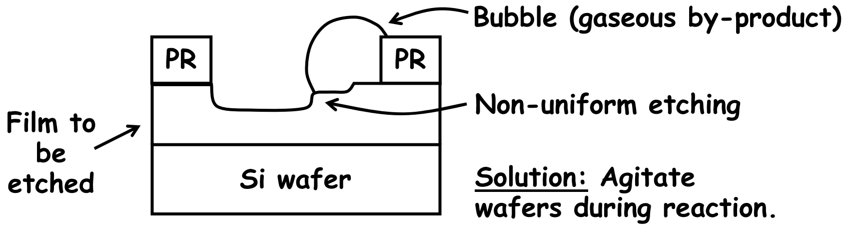
6. Incomplete wetting of the surface:



- For some etches (e.g., oxide etch using HF), the solution is to dip in DI water first, then into HF solution → the DI water wets the surface better

## Wet Etch Limitations (cont.)

7. Bubble formation (as a reaction by-product)
   - If bubbles cling to the surface → get nonuniform etching



**Solution:** Agitate wafers during reaction.

## Some Common Wet Etch Chemistries

**Wet Etching Silicon:**

**Common:** $Si + HNO_3 + 6HF \longrightarrow H_2SiF_6 + HNO_2 + H_2 + H_2O$

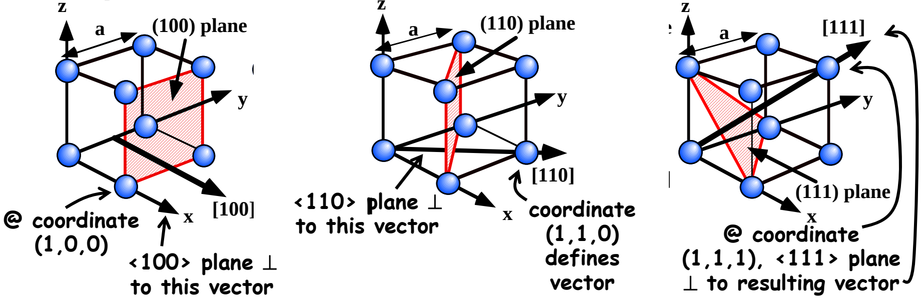
(isotropic)

(nitric acid) → (1) forms a layer of $SiO_2$

(hydrofluoric acid) → (2) etches away the $SiO_2$

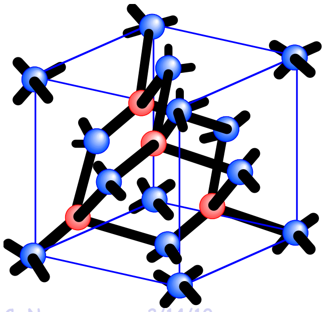
Different mixture combinations yield different etch rates.

## Silicon Crystal Orientation



- Silicon has the basic diamond structure
  - ↳ Two merged FCC cells offset by (a/4) in x, y, and z axes
  - ↳ From right:
    - # available bonds/cm² <111>
    - # available bonds/cm² <110>
    - # available bonds/cm² <100>

↑ Increasing



## Anisotropic Wet Etching

Anisotropic etches also available for single crystal Si:

- Orientation-dependent etching: <111>-plane more densely packed than <100>-plane

Faster E.R.

Slower E.R.

…in some solvents

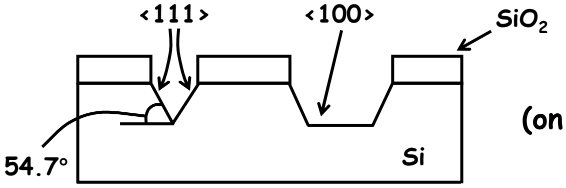
One such solvent: KOH + isopropyl alcohol

(e.g., 23.4 wt% KOH, 13.3 wt% isopropyl alcohol, 63 wt% $H_2O$)

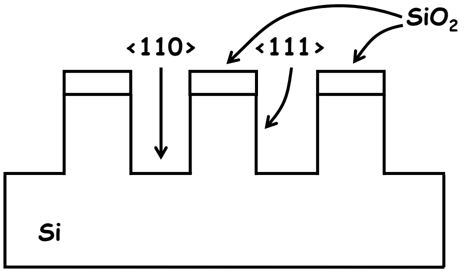
$\Longrightarrow$ $E.R._{\langle 100 \rangle} = 100 \times E.R._{\langle 111 \rangle}$

## Anisotropic Wet Etching (cont.)

Can get the following:



(on a <100> - wafer)



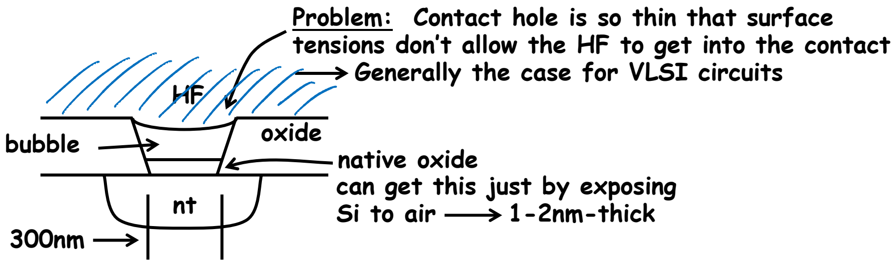
(on a <110> - wafer)

$\Longrightarrow$ Quite anisotropic!

## Wet Etching $SiO_2$

$$SiO_2 + 6HF \longrightarrow H_2 + SiF_6 + 2H_2O$$

Generally used to clear out residual oxides from contacts



**Problem:** Contact hole is so thin that surface tensions don't allow the HF to get into the contact → Generally the case for VLSI circuits

native oxide can get this just by exposing Si to air → 1-2nm-thick

**Solution:** add a surfactant (e.g., Triton X) to the BHF before the contact clear etch

1. Improves the ability of HF to wet the surface (hence, get into the contact)
2. Suppresses the formation of etch by-products, which otherwise can block further reaction if by-products get caught in the contact

## More Wet Etch Chemistries

- Wet etching silicon nitride
  - Use hot phosphoric acid: 85% phosphoric acid @ 180°C
  - Etch rate ~ 10 nm/min (quite slow)
  - **Problem**: PR lifted during such etching
  - **Solution**: use $SiO_2$ as an etch mask (E.R. ~2.5 nm/min)
    - ☛ A hassle → dry etch processes more common than wet
- Wet etchining aluminum
  - Typical etch solution composition:

80% phoshporic acid, 5% nitric acid, 5% acetic acid, 10% water

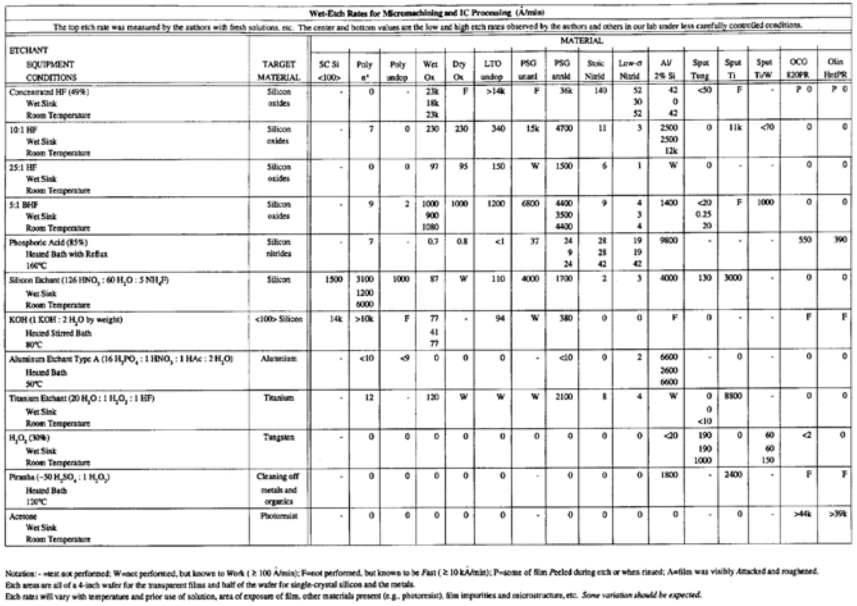
$(H_2PO_4)$ $(HNO_3)$ $(CH_3COOH)$ $(H_2O)$

(1) Forms $Al_2O_3$ (aluminum oxide)

(2) Dissolves the $Al_2O_3$

- **Problem**: $H_2$ gas bubbles adhere firmlly to the surface → delay the etch → need a 10-50% overetch time
- **Solution**: mechanical agitation, periodic removal of wafers from etching solution

## Wet Etch Rates (f/ K. Williams)



**Wet-Etch Rates for Micromachining and IC Processing (Å/min)**

The top etch rate was measured by the authors with fresh solutions, etc. The center and bottom values are the low and high etch rates observed by the authors and others in our lab under less carefully controlled conditions.

| ETCHANT<br>EQUIPMENT<br>CONDITIONS | TARGET MATERIAL | MATERIAL | | | | | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | SC Si <100> | Poly n⁺ | Poly undop | Wet Ox | Dry Ox | LTO undop | PSG unanl | PSG annld | Stoic Nitrid | Low-σ Nitrid | Al/ 2% Si | Sput Tung | Sput Ti | Sput Ti/W | OCG 820PR | Olin HntPR |
| Concentrated HF (49%)<br>Wet Sink<br>Room Temperature | Silicon oxides | - | 0 | - | 23k<br>18k<br>23k | F | >14k | F | 36k | 140 | 52<br>30<br>52 | 42<br>0<br>42 | <50 | F | - | P 0 | P 0 |
| 10:1 HF<br>Wet Sink<br>Room Temperature | Silicon oxides | - | 7 | 0 | 230 | 230 | 340 | 15k | 4700 | 11 | 3 | 2500<br>2500<br>12k | 0 | 11k | <70 | 0 | 0 |
| 25:1 HF<br>Wet Sink<br>Room Temperature | Silicon oxides | - | 0 | 0 | 97 | 95 | 150 | W | 1500 | 6 | 1 | W | 0 | - | - | 0 | 0 |
| 5:1 BHF<br>Wet Sink<br>Room Temperature | Silicon oxides | - | 9 | 2 | 1000<br>900<br>1080 | 1000 | 1200 | 6800 | 4400<br>3500<br>4400 | 9 | 4<br>3<br>4 | 1400 | <20<br>0.25<br>20 | F | 1000 | 0 | 0 |
| Phosphoric Acid (85%)<br>Heated Bath with Reflux<br>160°C | Silicon nitrides | - | 7 | - | 0.7 | 0.8 | <1 | 37 | 24<br>9<br>24 | 28<br>28<br>42 | 19<br>19<br>42 | 9800 | - | - | - | 550 | 390 |
| Silicon Etchant (126 $HNO_3$ : 60 $H_2O$ : 5 $NH_4F$)<br>Wet Sink<br>Room Temperature | Silicon | 1500 | 3100<br>1200<br>6000 | 1000 | 87 | W | 110 | 4000 | 1700 | 2 | 3 | 4000 | 130 | 3000 | - | 0 | 0 |
| KOH (1 KOH : 2 $H_2O$ by weight)<br>Heated Stirred Bath<br>80°C | <100> Silicon | 14k | >10k | F | 77<br>41<br>77 | - | 94 | W | 380 | 0 | 0 | F | 0 | - | - | F | F |
| Aluminum Etchant Type A (16 $H_3PO_4$ : 1 $HNO_3$ : 1 HAc : 2 $H_2O$)<br>Heated Bath<br>50°C | Aluminum | - | <10 | <9 | 0 | 0 | 0 | - | <10 | 0 | 2 | 6600<br>2600<br>6600 | - | 0 | - | 0 | 0 |
| Titanium Etchant (20 $H_2O$ : 1 $H_2O_2$ : 1 HF)<br>Wet Sink<br>Room Temperature | Titanium | - | 12 | - | 120 | W | W | W | 2100 | 8 | 4 | W | 0<br>0<br><10 | 8800 | - | 0 | 0 |
| $H_2O_2$ (30%)<br>Wet Sink<br>Room Temperature | Tungsten | - | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | <20 | 190<br>190<br>1000 | 0 | 60<br>60<br>150 | <2 | 0 |
| Piranha (~50 $H_2SO_4$ : 1 $H_2O_2$)<br>Heated Bath<br>120°C | Cleaning off metals and organics | - | 0 | 0 | 0 | 0 | 0 | - | 0 | 0 | 0 | 1800 | - | 2400 | - | F | F |
| Acetone<br>Wet Sink<br>Room Temperature | Photoresist | - | 0 | 0 | 0 | 0 | 0 | - | 0 | 0 | 0 | 0 | - | 0 | - | >44k | >39k |

Notation: - =test not performed; W=not performed, but known to Work ( ≥ 100 Å/min); F=not performed, but known to be *Fast* ( ≥ 10 kÅ/min); P=some of film *Peeled* during etch or when rinsed; A=film was visibly *Attacked* and roughened.
Etch areas are all of a 4-inch wafer for the transparent films and half of the wafer for single-crystal silicon and the metals.
Etch rates will vary with temperature and prior use of solution, area of exposure of film, other materials present (e.g., photoresist), film impurities and microstructure, etc. *Some variation should be expected.*

## Film Etch Chemistries

- For some popular films:

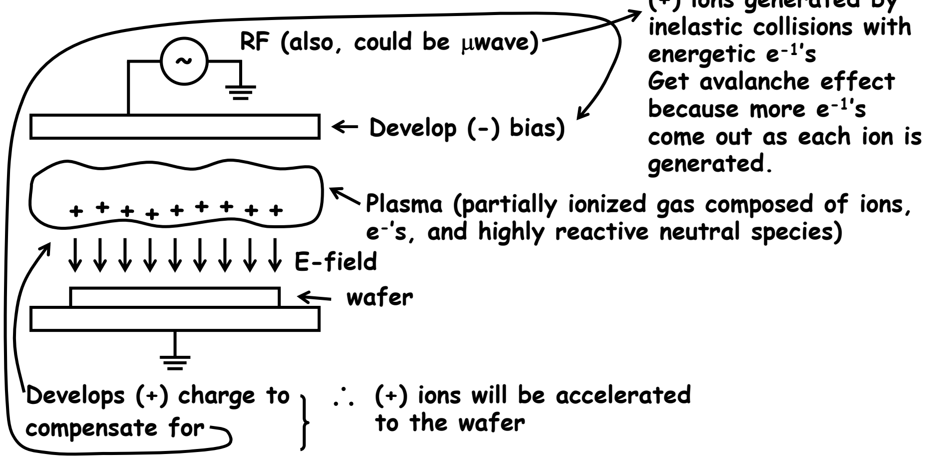
| Material | Wet etchant | Etch rate [nm/min] | Dry etchant | Etch rate [nm/min] |
|---|---|---|---|---|
| Polysilicon | $HNO_3$:$H_2O$:$NH_4F$ | 120-600 | $SF_6$ + He | 170-920 |
| Silicon nitride | $H_3PO_4$ | 5 | $SF_6$ | 150-250 |
| Silicon dioxide | HF | 20-2000 | $CHF_3$ + $O_2$ | 50-150 |
| Aluminum | $H_3PO_4$:$HNO_3$:$CH_3COOH$ | 660 | $Cl_2$ + $SiCl_4$ | 100-150 |
| Photoresist | Acetone | >4000 | $O_2$ | 35-3500 |
| Gold | KI | 40 | n/a | n/a |

# Dry Etching

## Dry Etching

- Physical sputtering
- Plasma etching
- Reactive ion etching

} All based upon plasma processes.



RF (also, could be μwave)

(+) ions generated by inelastic collisions with energetic $e^{-1}$'s
Get avalanche effect because more $e^{-1}$'s come out as each ion is generated.

← Develop (-) bias)

Plasma (partially ionized gas composed of ions, $e^{-}$'s, and highly reactive neutral species)

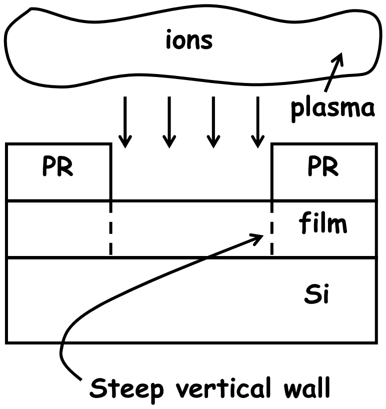
E-field

wafer

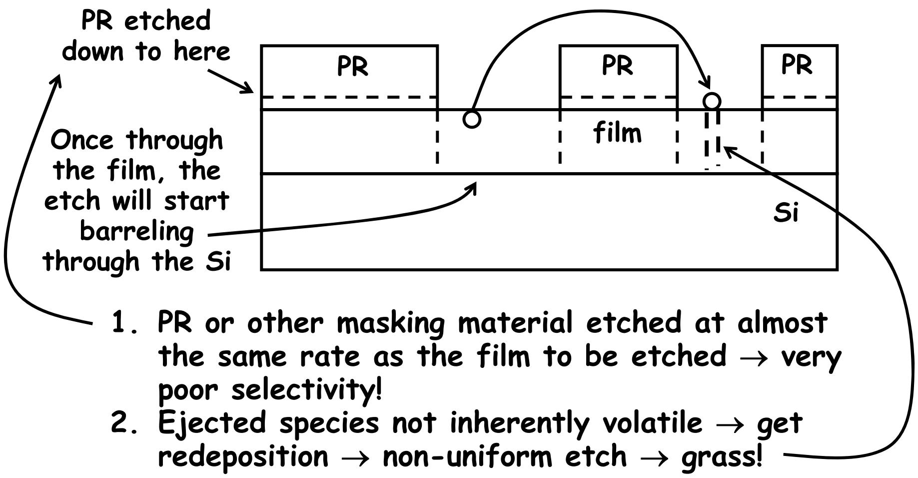
Develops (+) charge to compensate for } ∴ (+) ions will be accelerated to the wafer

## Physical Sputtering (Ion Milling)

- Bombard substrate w/ energetic ions → etching via physical momentum transfer
- Give ions energy and directionality using E-fields
- Highly directional → very anisotropic



## Problems With Ion Milling



1. PR or other masking material etched at almost the same rate as the film to be etched → very poor selectivity!
2. Ejected species not inherently volatile → get redeposition → non-uniform etch → grass!

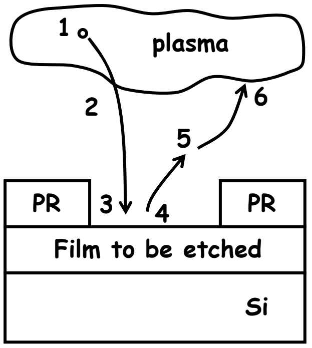
- Because of these problems, ion milling is not used often (very rare)

## Plasma Etching

- Plasma (gas glow discharge) creates reactive species that chemically react w/ the film in question
- Result: much better selectivity, but get an isotropic etch

Plasma Etching Mechanism:

1. Reactive species generated in a plasma.
2. Reactive species diffuse to the surface of material to be etched.
3. Species adsorbed on the surface.
4. Chemical reaction.
5. By-product desorbed from surface.
6. Desorbed species diffuse into the bulk of the gas



← MOST IMPORTANT STEP! (determines whether plasma etching is possible or not.)

## Ex: Polysilicon Etching w/ $CF_4$ and $O_2$

$$CF_4 \xrightarrow[\text{plasma}]{} CF_4^+ + CF_3^+ + CF_2^+ + CF^+ + F^+ + F^0 + CF_2^+ + \ldots$$

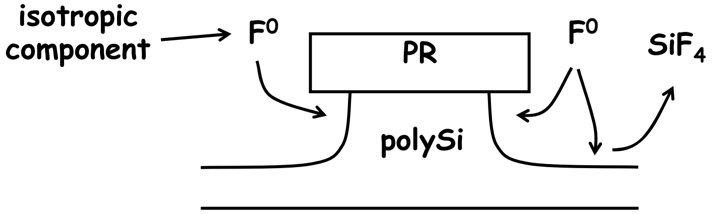
Neutral radical (highly reactive!)

Si

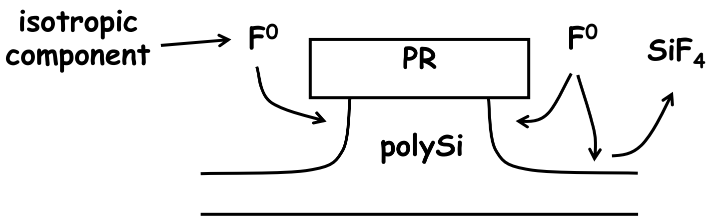
$$e^- + CF_4 \rightarrow CF_3 + F + e^-$$

$SiCF_6$, $SiF_4$ ← both volatile ∴ dry etching is possible.

- F° is the dominant reactant → but it can't be given a direction → thus, get isotropic etch!



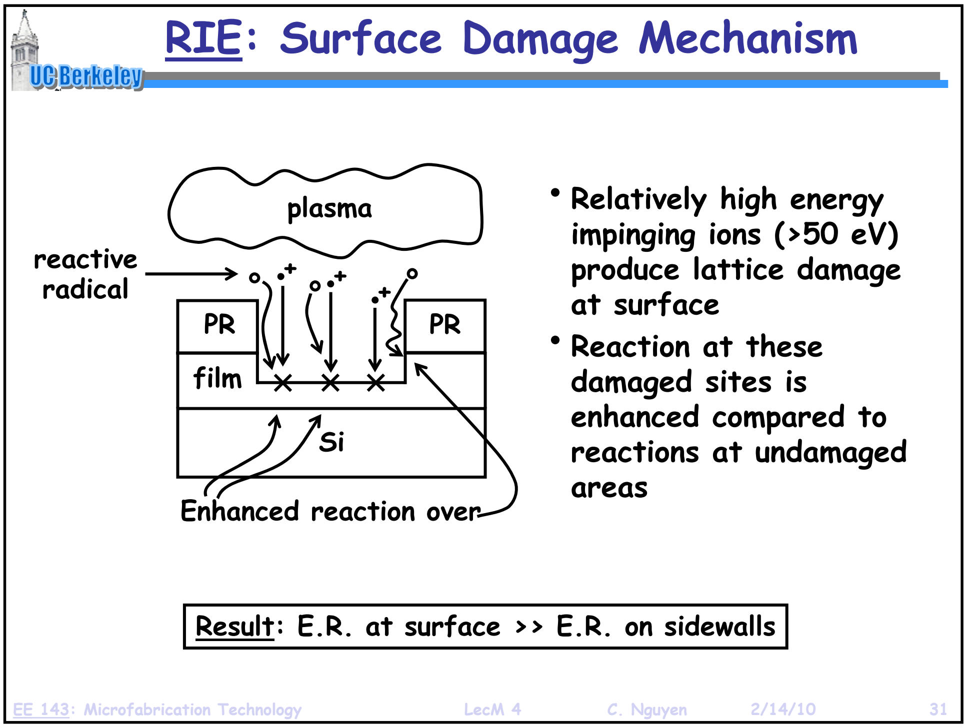
## Ex: Polysilicon Etching w/ $CF_4$ and $O_2$



- **Problems**:
    1. Isotropic etching
    2. Formation of polymer because of C in $CF_4$
        ↳ **Solution**: add $O_2$ to remove the polymer (but note that this reduces the selectivity, $S_{poly/PR}$)
- **Solution**:
    ↳ Use Reactive Ion Etching (RIE)

## Reactive Ion Etching (RIE)

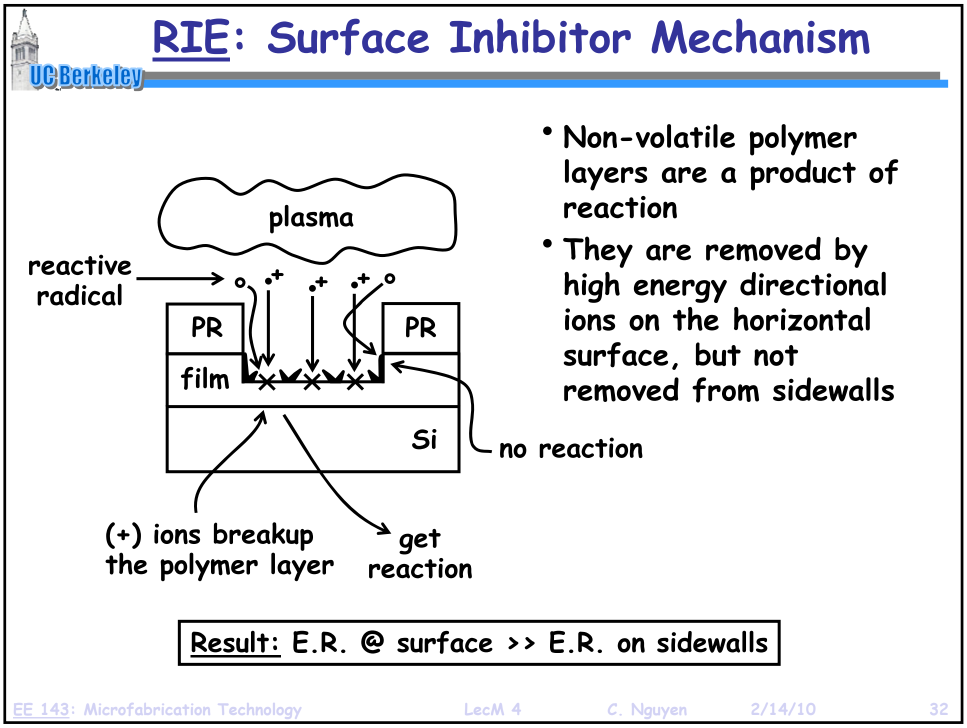
- Use ion bombardment to aid and enhance reactive etching in a particular direction
    ↳ **Result**: directional, anisotropic etching!
- RIE is somewhat of a misnomer
    ↳ It's not ions that react … rather, it's still the neutral species that dominate reaction
    ↳ Ions just enhance reaction of these neutral radicals in a specific direction
- Two principle postulated mechanisms behind RIE
    1. Surface damage mechanism
    2. Surface inhibitor mechanism



## RIE: Surface Damage Mechanism

- Relatively high energy impinging ions (>50 eV) produce lattice damage at surface
- Reaction at these damaged sites is enhanced compared to reactions at undamaged areas

**Result**: E.R. at surface >> E.R. on sidewalls



## RIE: Surface Inhibitor Mechanism

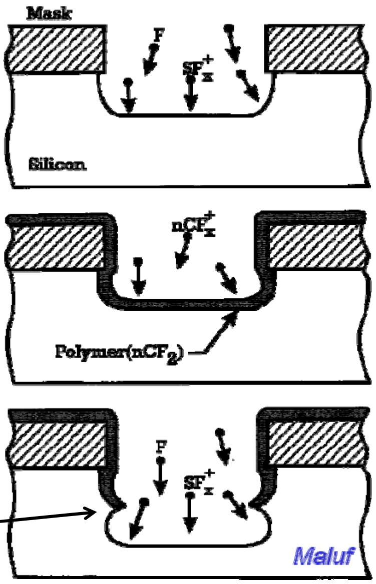
- Non-volatile polymer layers are a product of reaction
- They are removed by high energy directional ions on the horizontal surface, but not removed from sidewalls

**Result:** E.R. @ surface >> E.R. on sidewalls

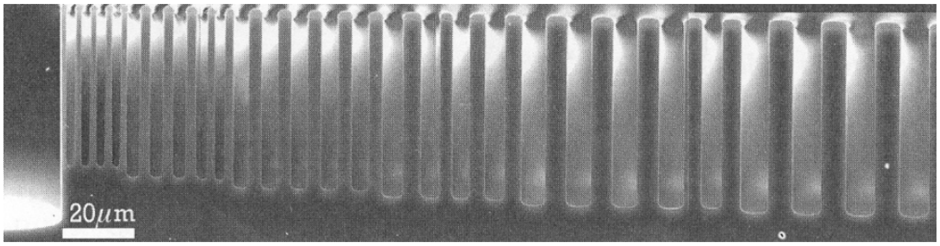
# Deep Reactive-Ion Etching (DRIE)

The Bosch process:

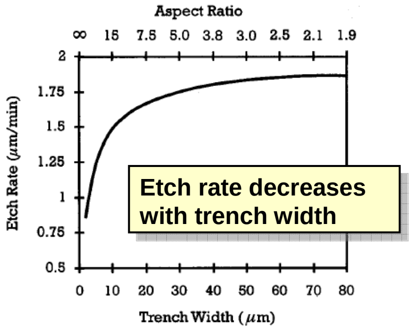
- Inductively-coupled plasma
- Etch Rate: 1.5-4 μm/min
- Two main cycles in the etch:
  - Etch cycle (5-15 s): $SF_6$ ($SF_x^+$) etches Si
  - Deposition cycle: (5-15 s): $C_4F_8$ deposits fluorocarbon protective polymer $(CF_2^-)_n$
- Etch mask selectivity:
  - $SiO_2$ ~ 200:1
  - Photoresist ~ 100:1
- Issue: finite sidewall roughness
  - scalloping < 50 nm
- Sidewall angle: 90° ± 2°



# DRIE Issues: Etch Rate Variance



- Etch rate is diffusion-limited and drops for narrow trenches
  - Adjust mask layout to eliminate large disparities
  - Adjust process parameters (slow down the etch rate to that governed by the slowest feature)



Etch rate decreases with trench width