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Basic Nanotechnology Processes

E SC 212

Unit 3
An Introduction to Wet Etching

Lecture 1
Wet Etching

Outline

- Introduction & Definitions
- Isotropic vs. Anisotropic Etching
- Wet Etch Parameters and Limitations
- Examples of Etch Profiles
- Wet Etch Recipes

Introduction

Definition of etching: The process of selectively removing material by chemical, electrolytic, or physical means.

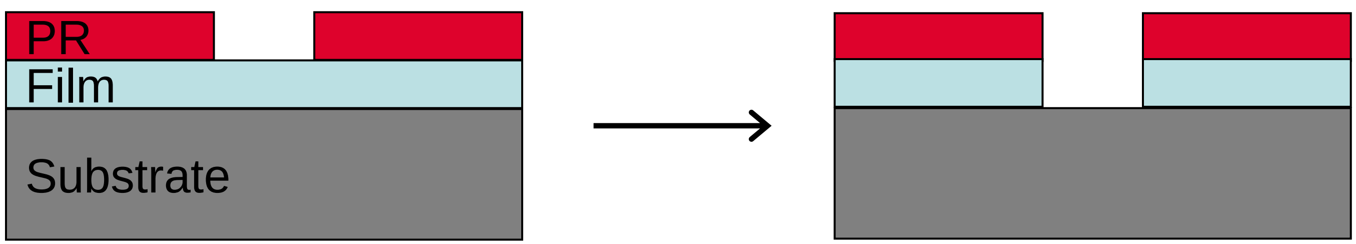
Chemical = a.k.a. “chemistry,” chemical reactions to convert solid material into soluble products.

Physical = bombardment, as in dry etching

Introduction

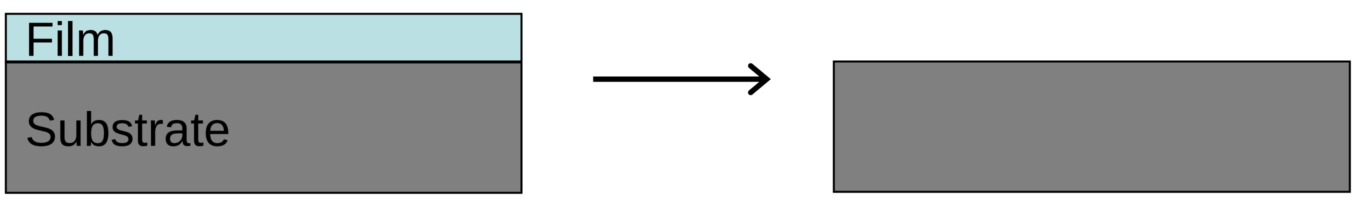
Etching is used to remove material from selected regions:

- The regions may be dictated by patterning, such as a photoresist pattern that was previously made with photolithography.



Idealized Case

- Or the region could be an entire wafer or substrate, as in the wet stripping of an entire blanket layer.



Types of Etching

There are two types of etching:

- Wet etching
  - Uses liquid chemicals to etch.
  - Usually creates a unique isotropic profile.
  - Uses only chemistry to etch.
- Dry etching
  - Uses plasma to etch.
  - Creates a more ideal etch (can create isotropic or anisotropic).
  - Uses both chemistry and bombardment to etch.

Introduction

<u>Etch vs. Dissolve</u>

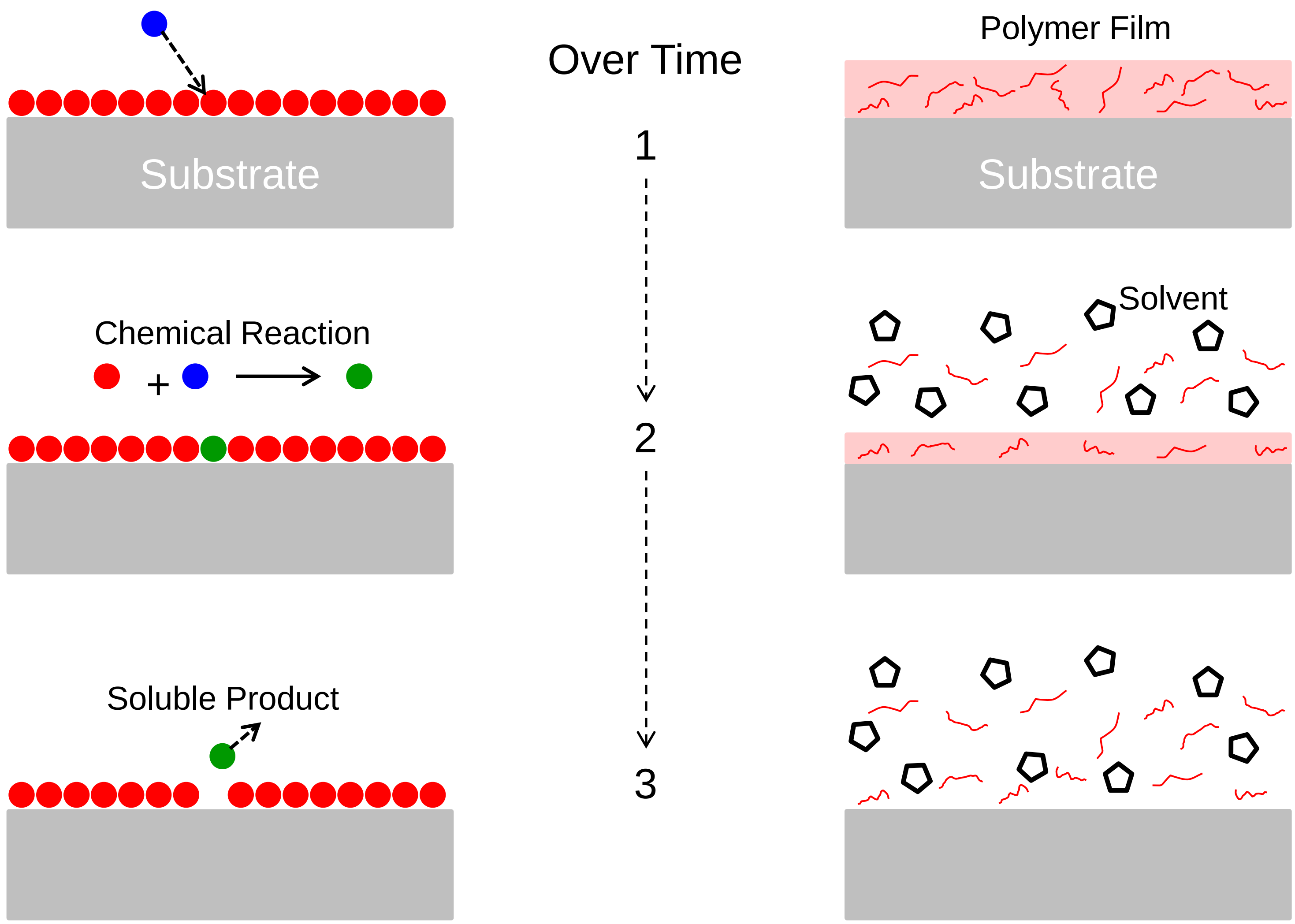
(with respect to wet chemistry)

Etch: a chemical reaction takes place to convert the film into a soluble product.

Dissolve: no chemical reaction is necessary. A good solvent is used to bring the material into solution without undergoing a chemical reaction.

Note: these terms are sometimes used interchangeably in nanofab processes.

Introduction



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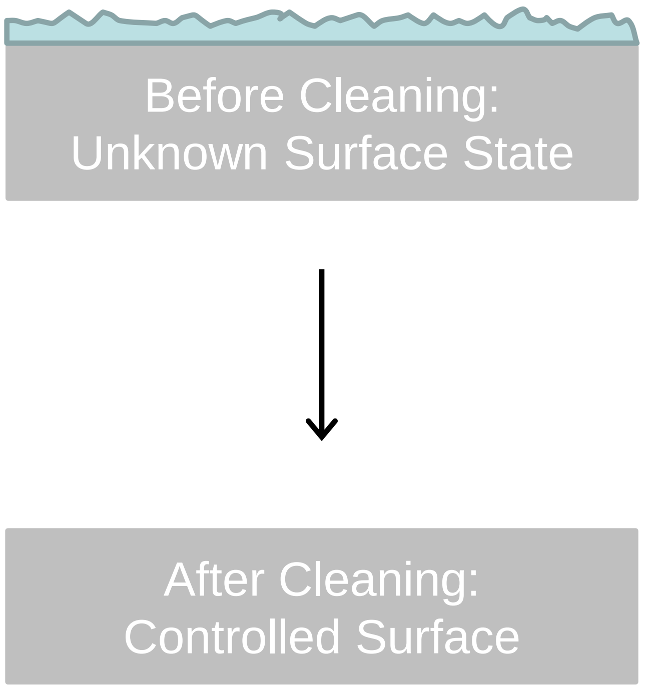
Introduction

- Cleaning may also be considered as wet a type of wet etching.
- In this case, the materials being etched away include unwanted residues (organics, metals, etc.) and particulate matter.
- Creates a controlled surface on which to build things (e.g., devices).



Example Cleaning Steps

Name	Components	Removes…
Piranha Mixture	Sulfuric Acid, Hydrogen Peroxide	Organics and Metals
SC1	Ammonium Hydroxide, Hydrogen Peroxide, Water	Particles and Organics
SC2	Hydrochloric Acid, Hydrogen Peroxide, Water	Metallic Residues
HF or BOE	Hydrofluoric acid, Buffer, Water	Native Oxide (SiO_2)

Proper cleaning generally involves many sequential steps and therefore can generate a significant volume of waste:

Piranha → Water → SC1 → Water → SC2 → Water → HF → Water → Drying

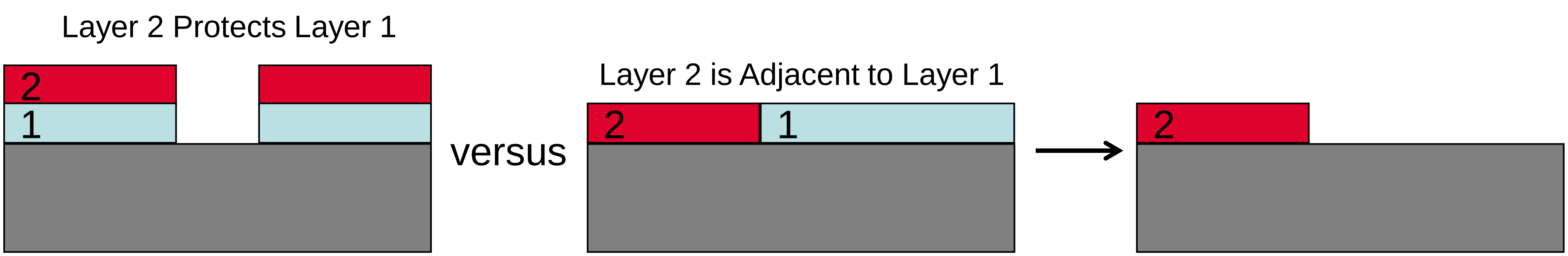
Figure of Merit: Etch Rate

- Etch Rate = thickness etched per time
- Usually desired rates are in the 10's to 100's of nm/min
- If rates are too high, may be difficult to control the process
- Too low of rates = long etch times

Figure of Merit: Selectivity

- The ability of an etchant to attack one material and not another.
- Wet chemical etching can be very selective, or not very selective depending upon the application.
- Represented as a ratio:

$$\text{Selectivity} = \frac{\text{Etch Rate of Material 1}}{\text{Etch Rate of Material 2}}$$



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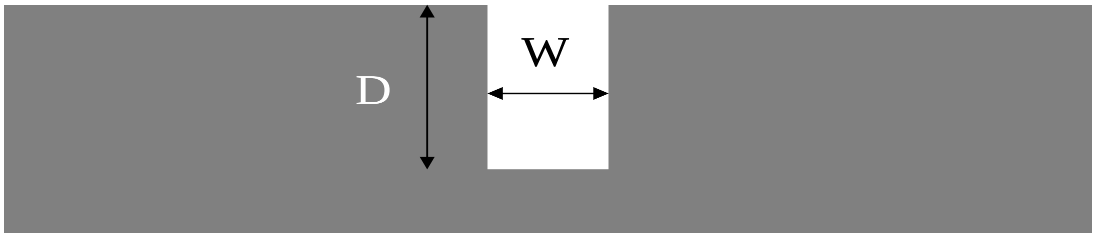
Aspect Ratio



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$$\text{Aspect Ratio} = \frac{D}{W}$$

Generally, high aspect ratios are harder to achieve than low ones.

High aspect ratio features are very desirable for many applications.

Due to its isotropic nature, it is difficult to obtain high aspect ratios with wet etching.

Dry etching is usually required to fabricate high aspect ratio features.

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- Introduction & Definitions
- Isotropic vs. Anisotropic Etching
- Wet Etch Parameters and Limitations
- Examples of Etch Profiles
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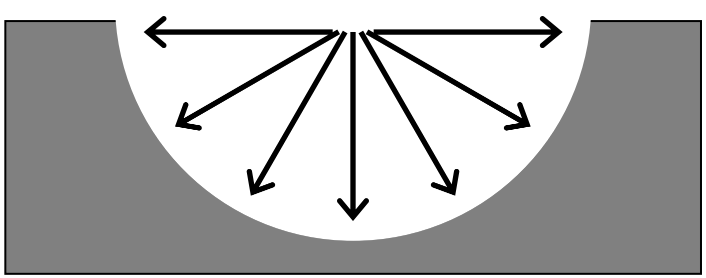
Isotropic vs. Anisotropic

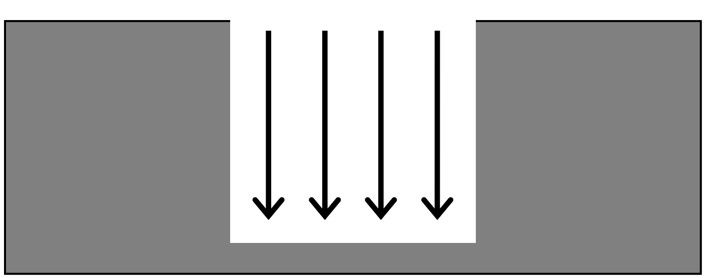
Isotropic: The same in all directions. Material is removed (etched) at the same rate in all directions (lateral and vertical).

Anisotropic: Directions are not equal. Etch rate in vertical direction is different from (greater than) etch rate in lateral direction.

<u>Isotropic</u>

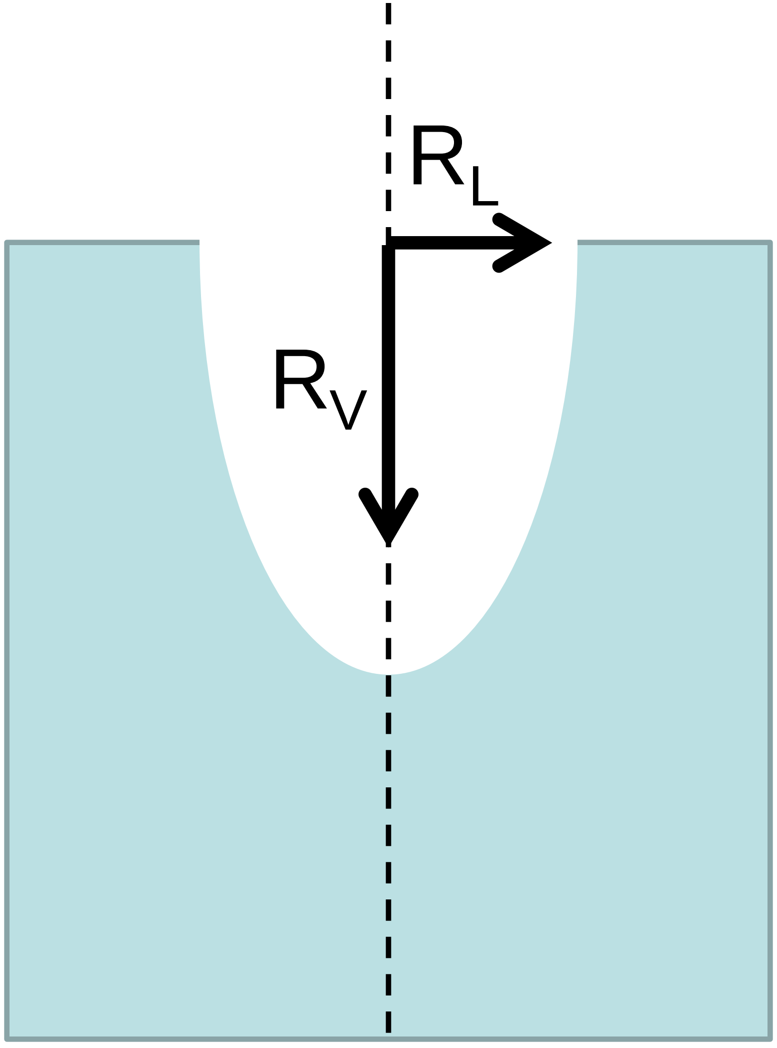


<u>Anisotropic</u>



Anisotropy

$$A = 1 - \frac{R_L}{R_V}$$



R_L = Lateral Etch Rate
R_V = Vertical Etch Rate

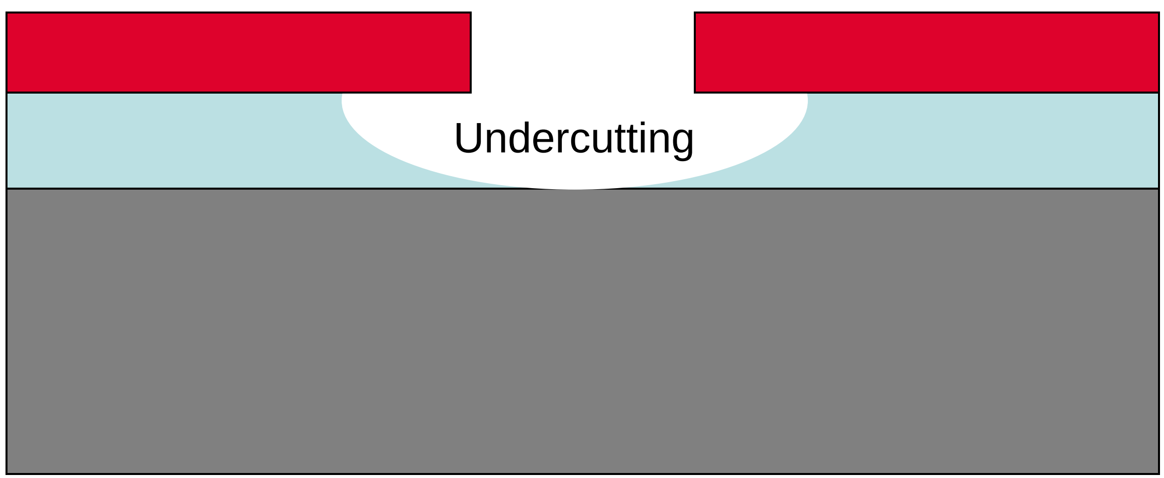
Isotropic

- Isotropic = the same in all directions
  - $R_L = R_V$
  - Characteristic wet etch profile.
  - Tends to undercut during etching.
  - Strictly chemical etching.
  - No physical energy component.

Pure Isotropic Etching

$$R_L = R_V$$

$$A = 1 - \frac{R_L}{R_V} = 1 - 1 = 0$$



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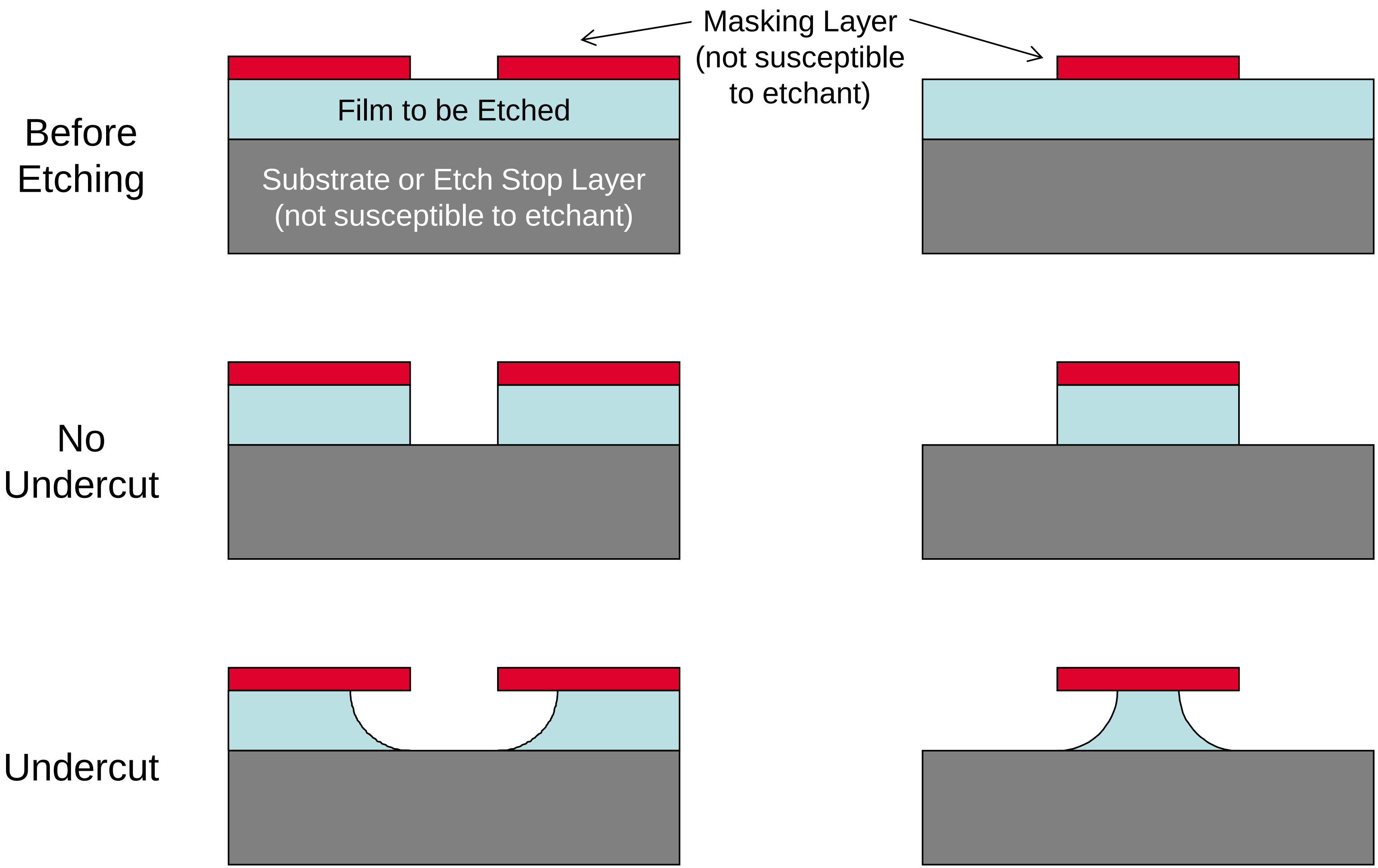
Undercut



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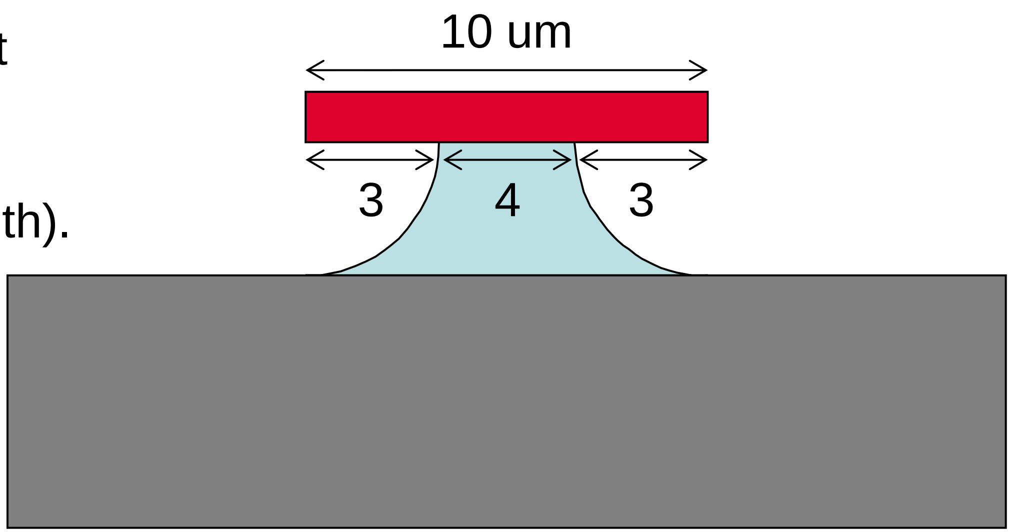
Undercut Example

Undercut: Lateral etching that occurs under the masking (protecting) layer.
Expressed as a distance (length).



Original Pattern Size = 10 um
Resulting Feature Size = 4 um
Undercut = 3 um each side

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Anisotropic

- Anisotropic: directions are not equal
- $R_V \neq R_L$, usually $R_V > R_L$
  - Commonly attained using dry etching.
  - Characteristic dry (plasma) etch profile, a function of chemistry and bombardment.
    - Chemistry – the chemical reactions that take place on the substrate.
    - Bombardment – kinetic ion energy directed at the substrate.

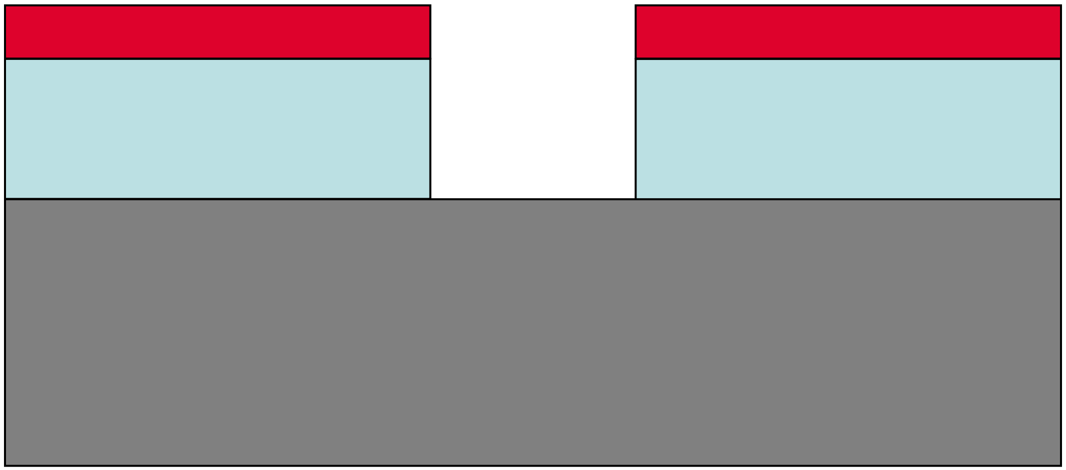
Anisotropic

- Anisotropic: directions are not equal
  - This type of profile can be achieved by some wet etches, in special cases.
  - Wet etchants etch some single crystal materials faster in certain crystallographic directions, resulting in anisotropic etch profiles.
  - Example: TMAH and KOH wet etching of silicon with certain crystal orientation.

Pure Anisotropic Etching

$$R_L = 0$$

$$A = 1 - \frac{R_L}{R_V} = 1 - 0 = 1$$



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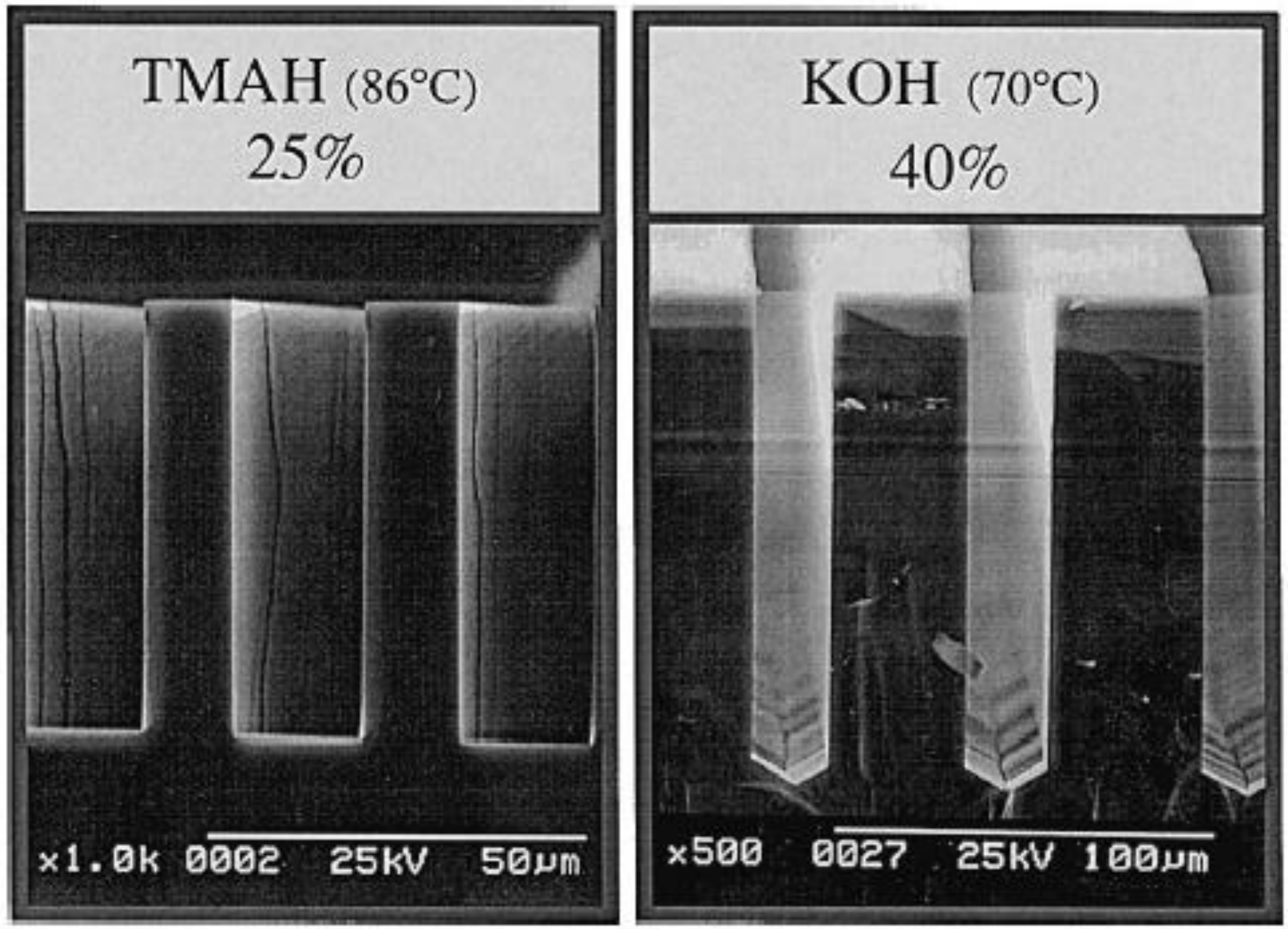
Anisotropic Silicon Wet Etches



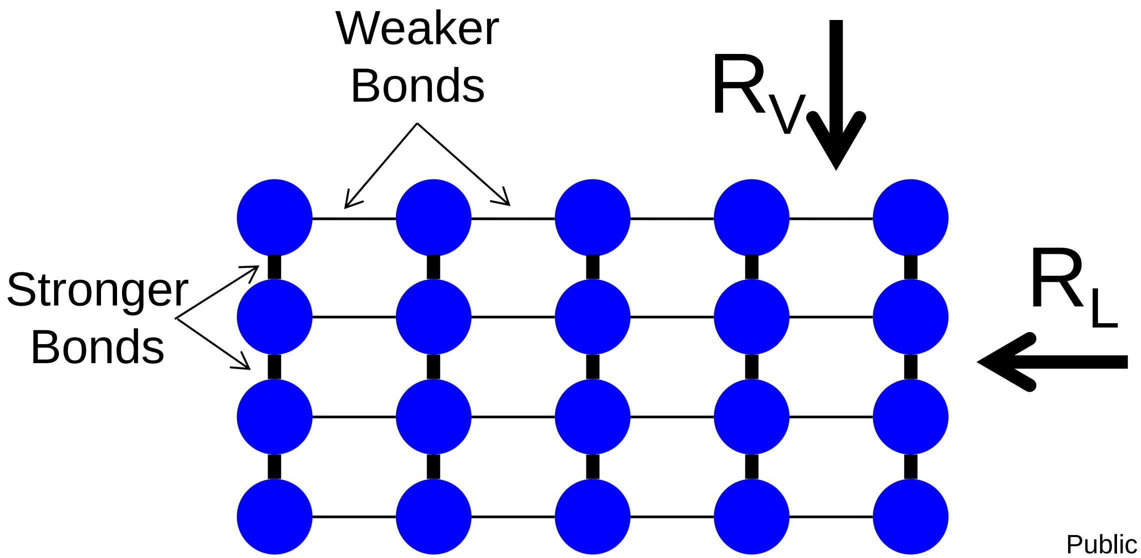
Actual etch profiles of deep grooves etched into a (110) or (100) silicon substrate using TMAH and KOH: (a) 26% TMAH 86°C; (b) 40% KOH 70°C

K. Sato et al.rSensors and Actuators 73(1999)131–137

Anisotropic Etching of Single Crystals

Crystal: a solid material consisting of very well-ordered atoms or molecules with a repeating pattern that extends in all three dimensions.

Directions and faces are not necessarily the same. Crystals may be anisotropic due to the packing arrangement of their constituent atoms or molecules.



In this idealized case:
$R_V > R_L$

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Wet vs. Dry Etching

Generally…

- Wet Etching: higher selectivity but lower anisotropy
- Dry Etching: lower selectivity but higher anisotropy

But…special conditions can exist which may give increased control over selectivity and/or anisotropy.

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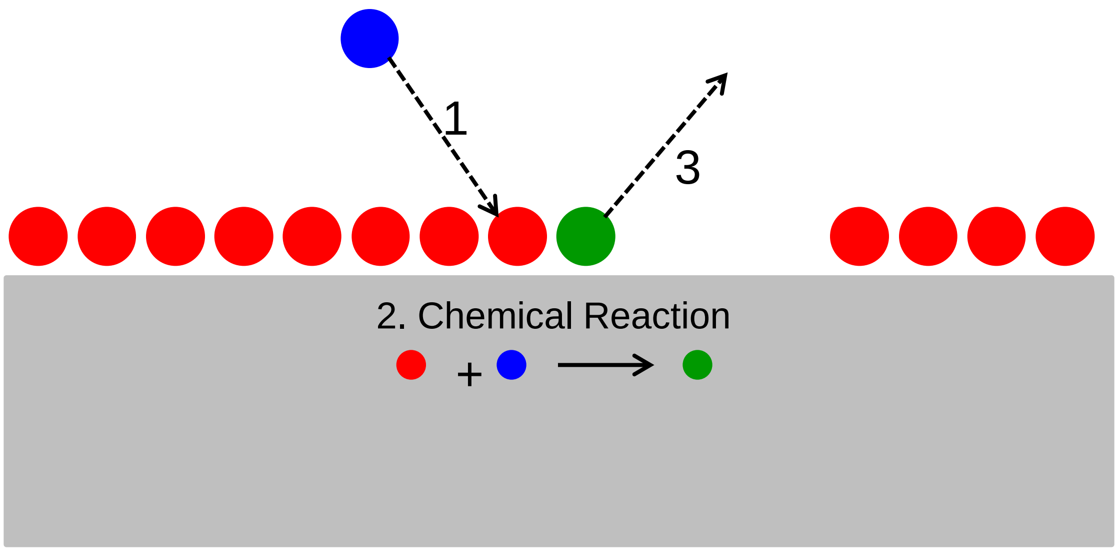
3 Steps of Wet Etching

1. Movement of etchant species to the surface of the sample
2. Chemical reaction with the exposed film (to form soluble products)
3. Movement of the reaction products away from the sample



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Rate Limiting Step

- The slowest step determines (limits) the overall etch rate.
- The slowest step in a process is called the rate limiting step.

Rate Limiting Step	**Remedy**
Transport of etchant to the surface of the film	Agitation, stirring, mixing, sonication
Chemical reaction between etchant and film	Heat
Transport of products away from the surface	Agitation, stirring, mixing, sonication

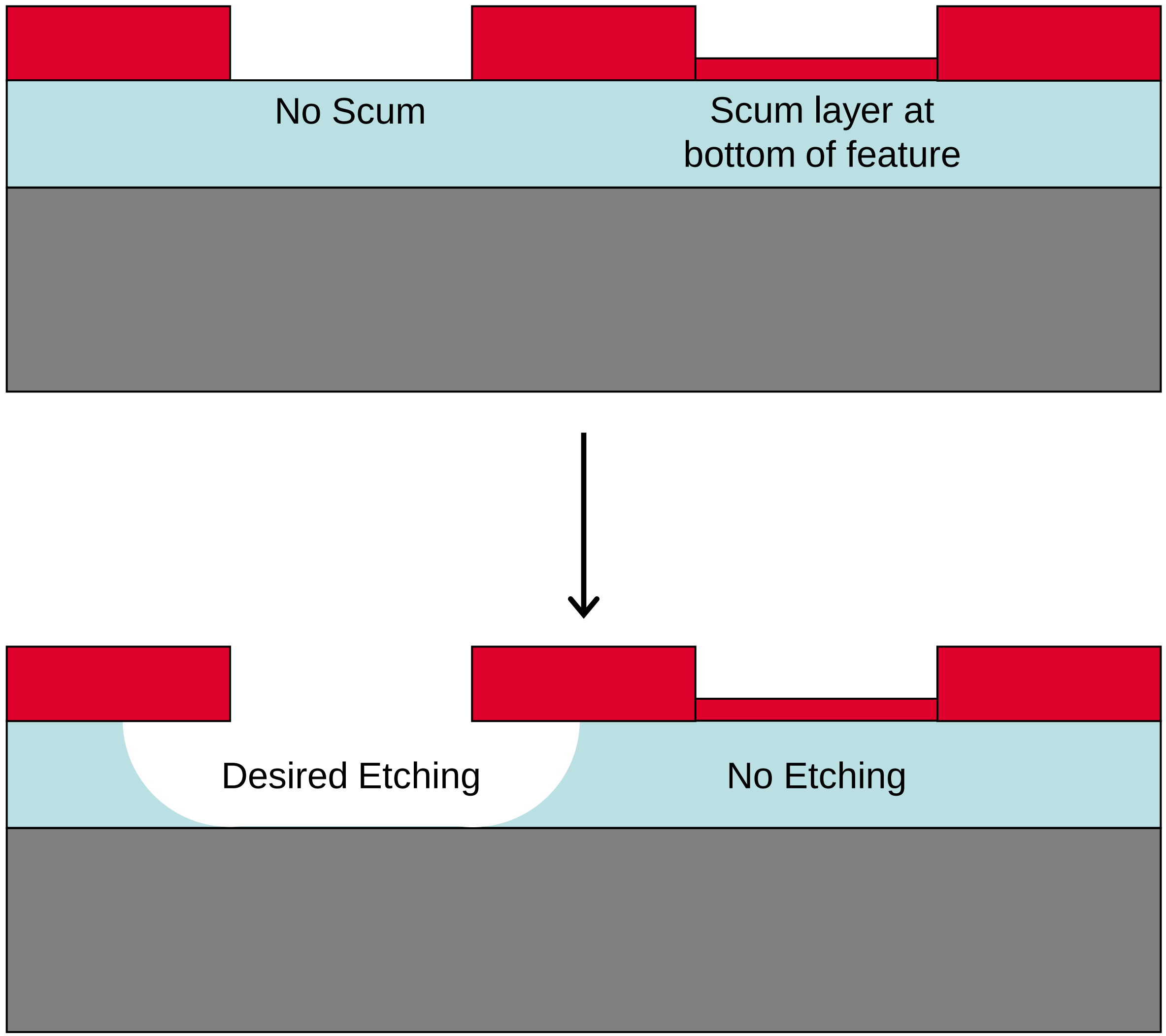
Wet Etching Parameters

Parameter	**Example**	**Comments**
Concentration	Molarity of acid in etch solution or ratio of components (etchant to buffer)	Changes over time as etchant is depleted and etch products are released into solution
Etch Time	Time of immersion in etch solution	Easy to control with digital timers
Temperature	Temperature of etch bath	Easy to control with heaters and thermostat
Agitation	Stirring or sonication (ultra- vs. mega-sonics)	Can be complicated to control. Depends of geometry of vessel and sample holders
Number of Runs	How many samples are etched at once? After how many batches is the solution changed?	Easy to control but requires bath composition to be analyzed

Common Problems in Wet Etching

- Bubbles can form and prevent good transport to/from the surface.
  - Sources of bubbles:
    - If the etch products are gases
    - Entrainment of bubbles due to vigorous agitation
- Resist scumming: incomplete development leaves a thin layer of photoresist that prevents etching.

Resist Scumming



Note: the top layer is chosen to be very resistant to etching.

Wet Etching Limitations

- Difficult to control
- Isotropic in nature (except special cases)
- High levels of defects (especially from particulates in the etch solution)
- Cannot be used for small features
- Practical limit = 2-3 um
- Produces large volumes of liquid waste

Other Etching Considerations

- Safety of the operator
- Damage to the sample or substrate
- Proper disposal of waste
- Environmental concerns

Wet Benches

- Wet benches are used to provide a safe and clean working environment.
- Generally wet benches are connected to an exhaust fan to draw hazardous fumes away from the user. The clear sash aids in containing fumes and prevents splashing.
- Typically the benches provide DI water, sinks, and storage for process chemicals.
- Benches are often segregated to prevent unwanted reactions between incompatible materials.

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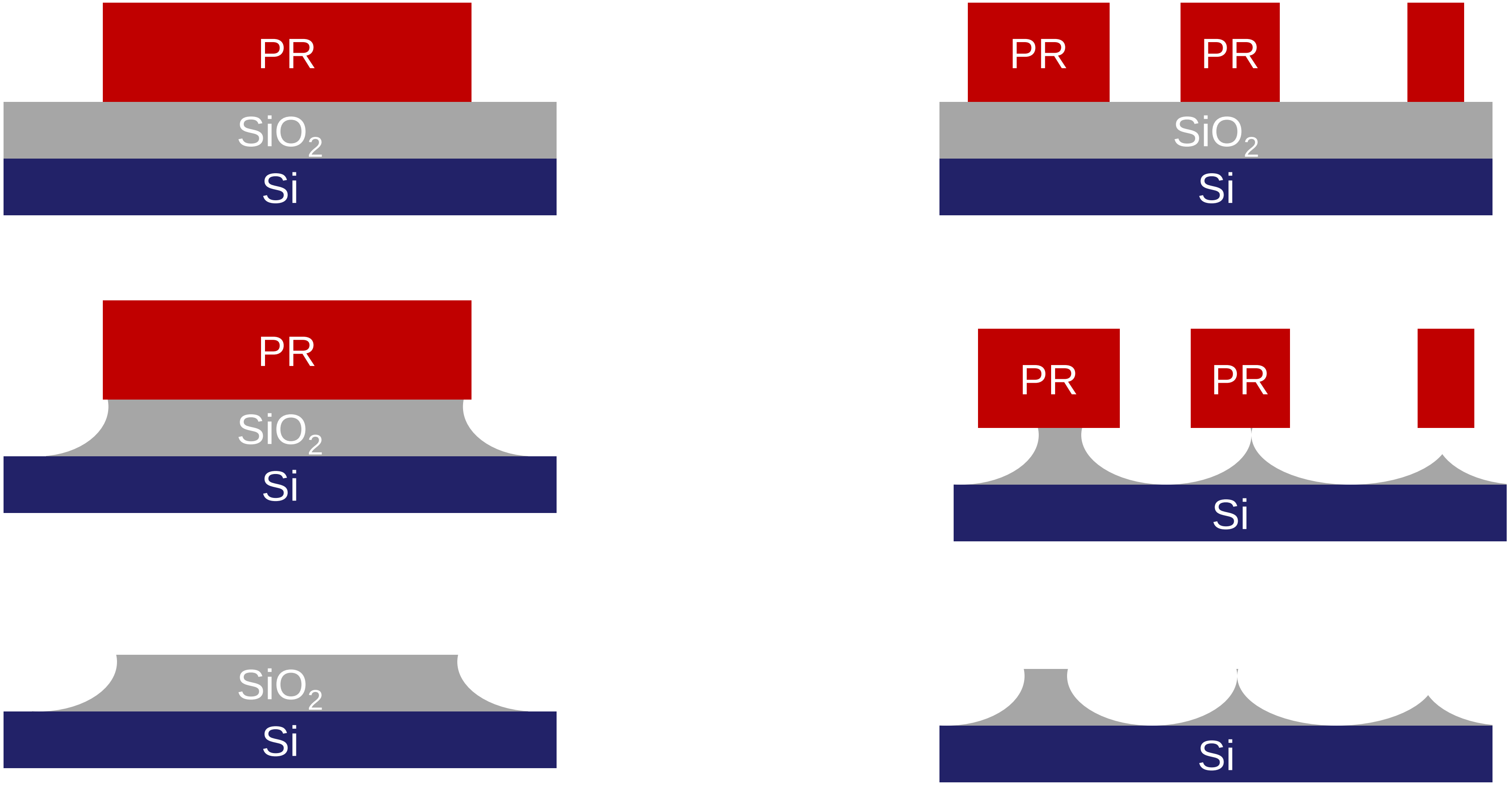
Isotropic Etch Profiles



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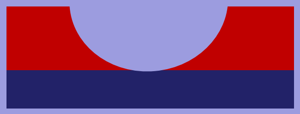
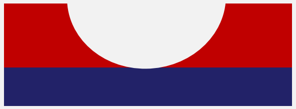
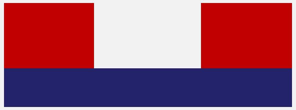
Sidewall Profiles

Types of etch	Sidewall Profile	Diagram
Wet Etch	Isotropic	
Dry Etch	Isotropic	
	Anisotropic	
	Anisotropic—Taper	
	Silicon trench	

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Wet Etch Selection

- Materials have varying etch rates in different etchants.
- For a particular target material, some chemistries will etch more efficiently than others.
- Increasing temperature will increase an etch rate for a specific chemistry.
- Temperature and chemistry are used to control selectivity.
- The following information provides general guidelines for etching various materials.

SiO_2

Wet Etchant	Concentration	Etch Temp	Relative Etch Rate
Hydrofluoric Acid HF*	2M	20^{o}C	500 Å/min
Buffered Oxide Etch $HF:NH_4F:H_2O$*	1:1:6	20^{o}C	2,000 Å/min
Acetic acid : Ammonium Fluoride $C_2H_4O_2$: NH_4F*	2:1	20^{o}C	1,000 Å/min

*Van Zant, Peter. Microchip Fabrication 4th ed. New York. 2000
+Runyan, W.R., Bean, K.E. Semiconductor Intergrated Circuit Processing Technology. New York. 1994

Hydrofluoric Acid

HF is the preferred wet etch for SiO_2. It can be used in several different forms:

- Undiluted HF (49% by wt)
- Buffered Oxide Etch (BOE): a diluted form of HF that uses ammonium fluoride to buffer the solution.

$$NH_4F \rightarrow NH_3 + HF$$

- The buffer maintains the supply of HF and provides control over pH (acidity or basicity)
- Common form: 6 parts buffer solution (40 wt% NH_4F in H_2O) to 1 part HF (49 wt% in H_2O)

Silicon

Wet Etchant	Concentration	Etch Temp	Relative Etch Rate
Nitric Acid & HF HNO_3:HF:*	5:1 HF	20°C	45 Å/min
$HF:H_2O_2:H_2O$*	1:1:6	20°C	1,000 Å/min

*Van Zant, Peter. Microchip Fabrication 4th ed. New York. 2000
+Runyan, W.R., Bean, K.E. Semiconductor Intergrated Circuit Processing Technology. New York. 1994

Si_3N_4

Wet Etchant	Concentration	Etch Temp	Relative Etch Rate
Buffered Oxide Etch $NH_4F/H_2O:HF/H_2O$*	6:1	20°C	600 Å/min
Phosphoric Acid H_3PO_4	80% solution in DI	150-180°C	80 Å/min
Phosphoric Acid: Nitric Acid: Acetic Acid: DI H_3PO_4: HNO_3: $C_2H_4O_2$:H_2O*	16:1:1:2	40-50°C	1,000 Å/min

*Van Zant, Peter. Microchip Fabrication 4th ed. New York. 2000
+Runyan, W.R., Bean, K.E. Semiconductor Intergrated Circuit Processing Technology. New York. 1994

Hot H_3PO_4 Etching

- The bath is kept at 150 – 180^oC.
- A selective etch for SiN_x vs SiO_2 (10:1).
- Difficult to control the bath, because of the high temperature of the chemicals.
- During the removal, some oxynitride is formed. A short HF deglaze may be necessary to remove the oxynitride before further processing.

Metal Etching

- Often metals are deposited over SiO_2 or Si_3N_4, since these common dielectrics provide electrical insulation.
- When metal etching, it is important to choose a chemistry that will effectively etch the metal, without attacking the underlying material.

Aluminum

Wet Etchant	Concentration	Etch Temp	Relative Etch Rate
Phosphoric Acid: Nitric Acid: Acetic Acid: DI H_3PO_4: HNO_3: C_2H_4O2 :H_2O *	16:1:1:2	40-50^oC	350Å/min
Hydrochloric Acid: Acetic Anhydride HCl: $(CH_3CO)_2O$ *	1:1	20^oC	3,000Å/min

*Kern, Werner. Chemical Etching. Princeton, NJ. 1978

Aluminum Etch

- Phosphoric acid, Nitric acid, Acetic acid
  - The most commonly used etch for aluminum.
  - Used because it can break through the Al_2O_3 layer to etch the Al beneath.
- HF can also be used to etch Al.

Platinum

Wet Etchant	Concentration	Etch Temp	Relative Etch Rate
Hydrochloric Acid: Nitric Acid: DI HCl: HNO_3: H_2O*	7:1:8	85^oC	400-500Å/min
Hydrochloric Acid+ HCl	3M	20^oC	1,000Å/min

*Kern, Werner. Chemical Etching. Princeton, NJ. 1978
+Runyan, W.R., Bean, K.E. Semiconductor Intergrated Circuit Processing Technology. New York. 1994

Gold

Wet Etchant	Concentration	Etch Temp	Relative Etch Rate
Potassium Iodide: Iodine KI: I_2: H_2O *	4:1:10	20°C	0.5 – 1 µm/min
Hydrochloric Acid: Nitric Acid HCl:HNO_3 *	3:1	30-40°C	25 – 30 µm/min
Potassium Ferricyanide: Potassium Cyanide: Potassium Hydroxide $K_3Fe(CN)_6$: KCN: KOH *	4:2:1	20°C	600 Å/min

*Kern, Werner. Chemical Etching. Princeton, NJ. 1978

Gold Etch

- Pre-mixed gold etch is used in our lab
  - Gold Etch TFA made by Transene Inc.
  - KI : I_2 : H_2O Solution
- Solution is opaque, so removal from solution is required to observe endpoint.

Chromium

Wet Etchant	Concentration	Etch Temp	Etch Rate
Ceric Ammonium Nitrate: Nitric Acid $H_8CeN_8O_{18}$: HNO_3 +	16:6	40^{o}C	2400Å/min
Sodium Hydroxide: Potassium Ferricynide NaOH: $K_3Fe(CN)_4$ *	1:3	20-40^{o}C	250-1,000Å/min
Ceric Sulfate : Nitric Acid $Ce(SO_4)_2$: HNO_3 *	9:1	20^{o}C	800 Å/min
Hydrochloric Acid HCl *	3M	20^{o}C	1,500 Å/min

*Kern, Werner. Chemical Etching. Princeton, NJ. 1978
+ http://www.transene.com/cr.html#1020

Chromium Etch

- Pre-mix used in lab
  - Chromium Etch 1020 made by Transene Inc.
  - $H_8CeN_8O_{18}$: HNO_3 Solution.
- Used for etching Cr masks and vacuum-deposited Cr in general.
- Photoresist mask can be used.
- Doesn’t require depassivation.

Vapor Etching

- Uses chemical vapor chemistry to etch rather than liquid chemistry.
- Requires heating of chemicals to produce the required vapor and prevent condensation.
- Most commonly used vapor is HF.
- Advantages:
    - Continued vapor replenishment at chemical/material interface.
    - More controllable than the standard dip etch procedure.
    - Instant etch termination.
- Disadvantages:
    - Material dependant.
    - Generally toxic vapors.
    - Must be contained in a closed system.