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Course: EE3013 Semiconductor Devices and Processing

School: School of Electrical and Electronic Engineering

Etching – Wet Etching

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Lesson Objectives - Etching

At the end of this lesson on etching, you should be able to:

- Explain the fundamental concepts of wet and dry etching
- Identify the factors determining the etch rate in wet and dry etching
- Explain the techniques to improve the etch rate in wet and dry etching

Standard Process Iteration

Three main categories in semiconductor fabrication process:

Lithography	Etching	Deposition
Patterning of substrate (silicon wafer)	Removal of materials from the substrate	Deposit materials (metal/ non-metal) on the substrate

Etching Techniques

Etching can be done either in **“wet”** or **“dry”** method:

Wet etching

- Wet etching is a process whereby materials are removed by liquid etchants.
- Wet etching is fast, cheap and simple, but harder to control. Hence, it is not popular in nanofabrication.

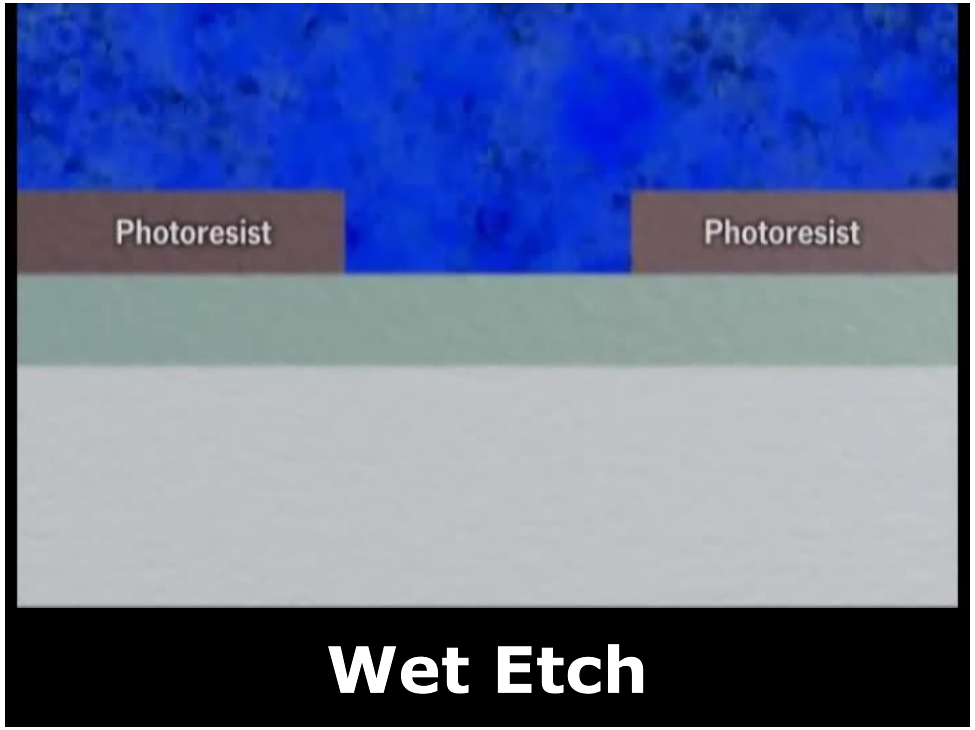
Dry etching

- Dry etch uses gas phase etchants in plasma.
- In comparison, dry etching is slower, requires sophisticated equipment, but easier to control.
- It works for many dielectric materials and some metals (Al, Ti, Cr, Ta, W, etc.).

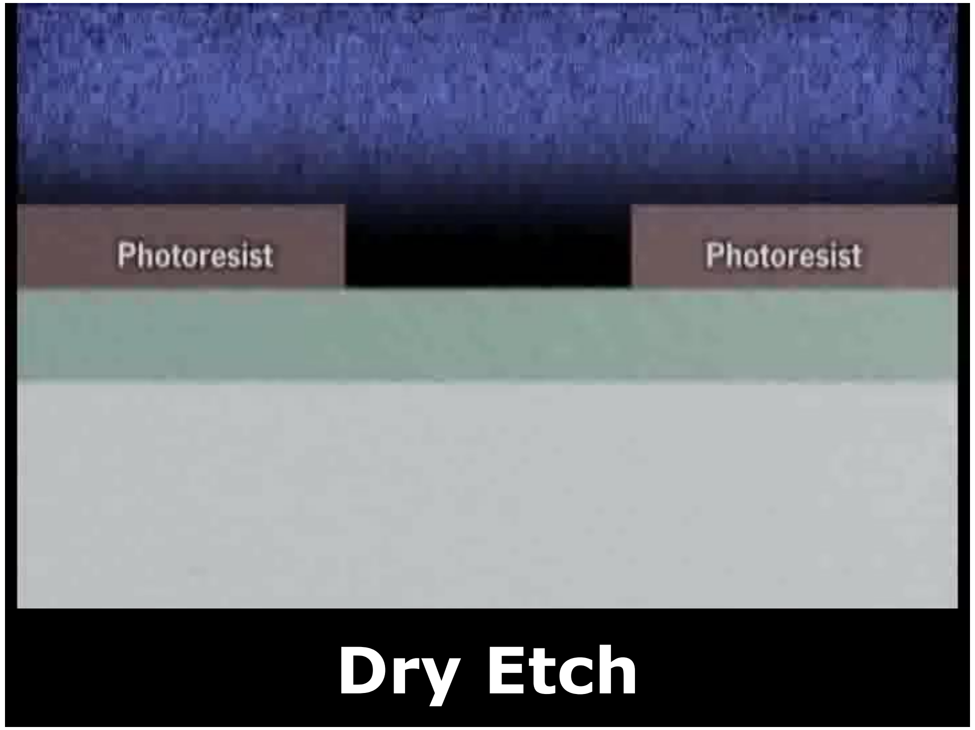
Types of Etch Profile

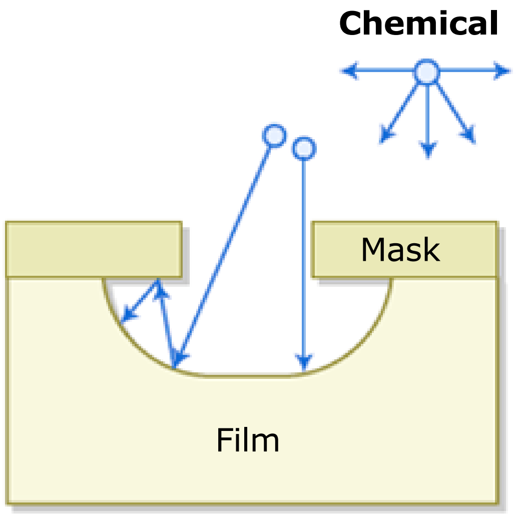
Two types of **Etch Profile**: **Isotropic** and **Anisotropic**

Isotropic Etching



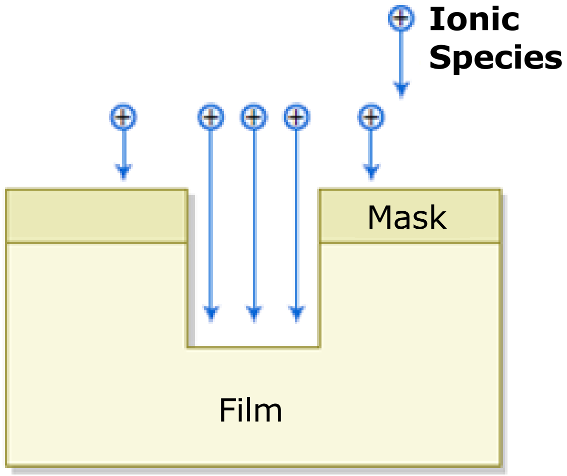
Anisotropic Etching





Isotropic etching

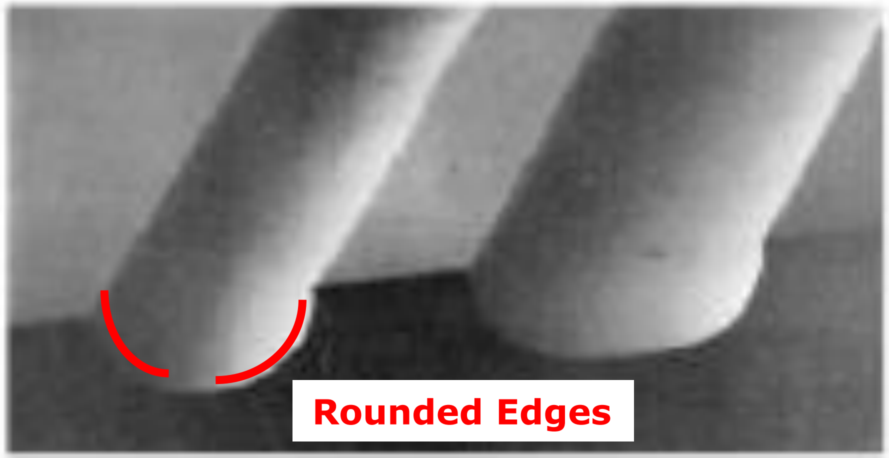
Attacks the materials equally in all directions and results in the undercut of the mask. Thus, the obtained feature size will be larger than the mask design.



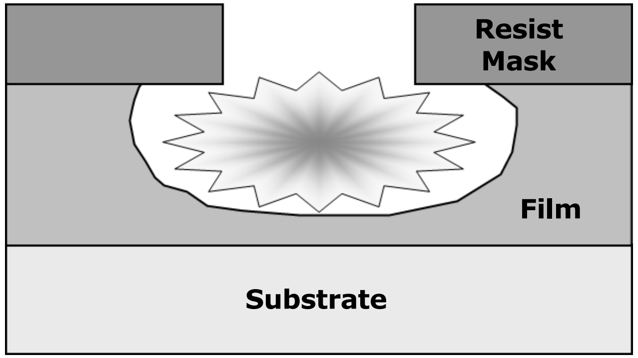
Anisotropic etching

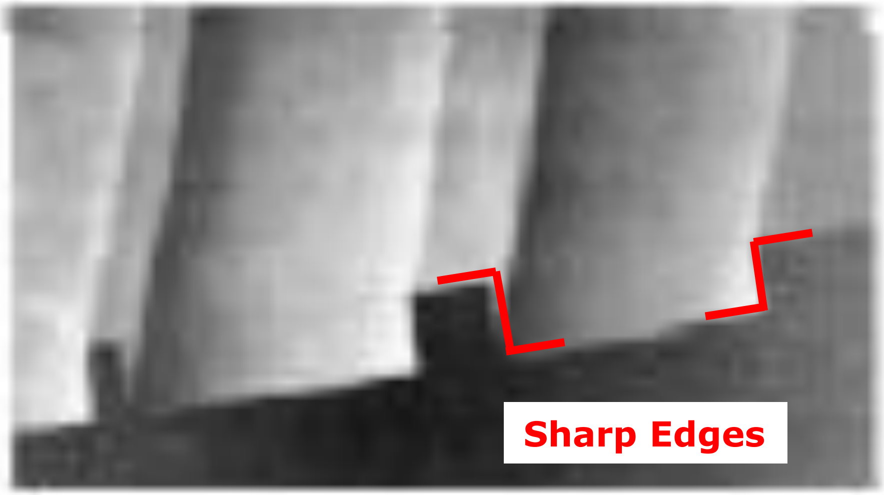
Etching rate is faster in vertical directions than horizontal directions, forming straight edge features.

Isotropic and Anisotropic Etching Profiles

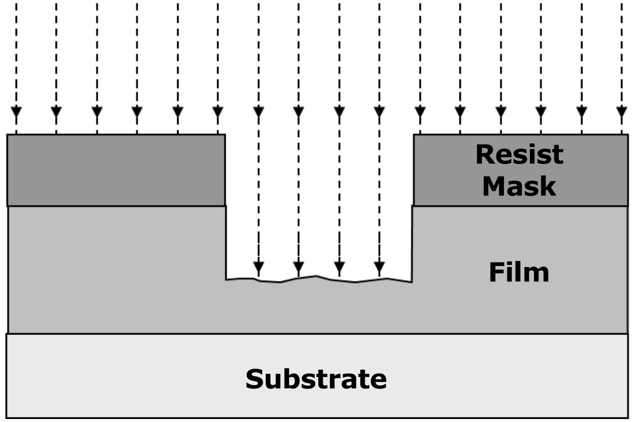


Isotropic etch:
Etches in all directions at the same rate





Anisotropic etch:
Etches in only one direction



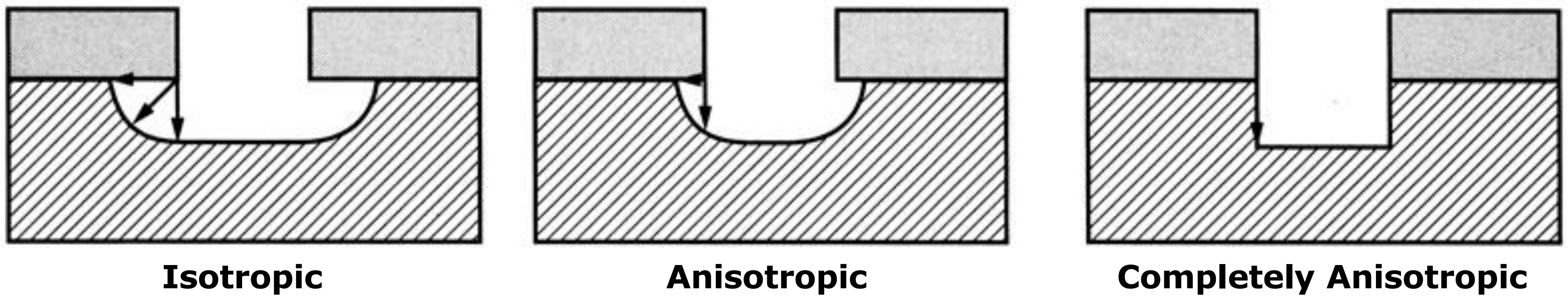
Figures of Merit: Degree of Anisotropy

In most etching techniques, there is a mixture of isotropic and anisotropic features.

Pause and observe carefully

Degree of Anisotropy: $A = 1 - \frac{R_L}{R_V}$

Where R_L is the lateral and R_V is the vertical etch rates respectively.



Isotropic: A=0

Increasing Degree of Anisotropic

Anisotropic: A=1

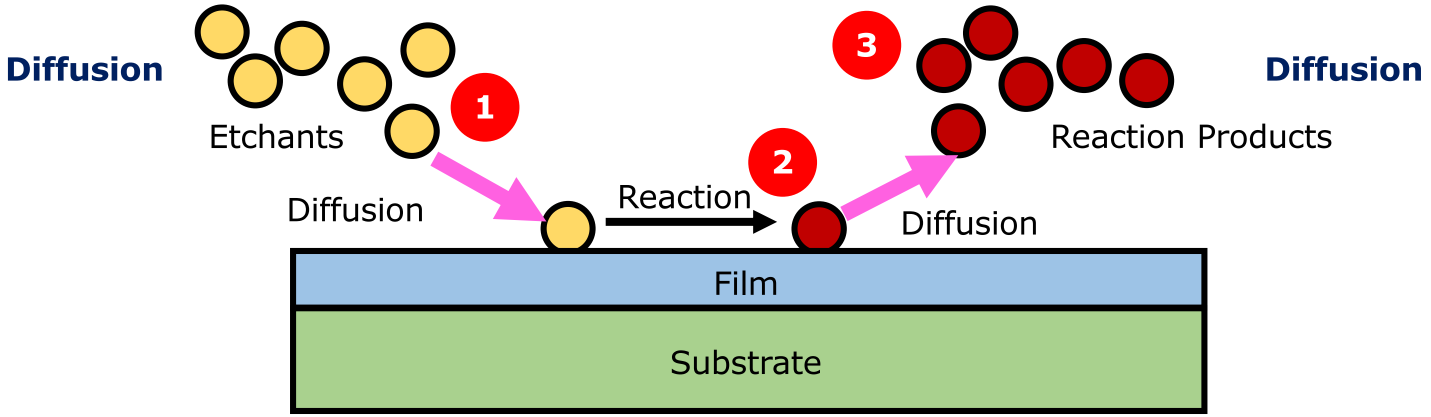
Wet Etching

Wet Etching Processes

Etching comprises of 3 sub-processes:

1. Etchants diffuse to the reacting surface
2. Chemical reaction at the surface
3. Removal of the products from the surface through diffusion

Pause and observe carefully



- It is desirable to have a large, uniformed and well-controlled etch rate.
- The overall etch rate is determined by the slowest sub-process, which is called a ***rate-limiting step***.
- The possible rate-limiting step in wet etching can either be step **(1)**, **(2) or (3)**.

Practice Question 1

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Select the most suitable technique to accelerate the corresponding sub-process.

Sub-Process in Wet Etching	Technique to Accelerate Sub-Process
(1) Etchants diffuse to the substrate surface	Etchant agitation / Etching in elevated temperature
(2) Chemical reaction at the surface	Etchant agitation / Etching in elevated temperature
(3) Removal of the products from the surface through diffusion	Etchant agitation / Etching in elevated temperature

Pause and attempt this question

Etchant agitation: Etching in an ultrasonic bath

Etchant agitation can effectively improve the diffusivity of etchants, hence accelerating process (1) and (3).

By etching in elevated temperature, the reaction rate between etchants and substrate's surface can be effectively improved, hence accelerating process (2).

Silicon Etching Process by HF and HNO_3

Silicon can be etched away by a mixture of **HNO_3** and **HF**, coupled with a diluent (water or acetic acid).

HNO_3 oxidises Si to form SiO_2.

HF will etch away the formed SiO_2.

Silicon Etching Process by HF and HNO_3

Pause and observe carefully

Local anodisation, oxidising the silicon (**holes** are required to start this process)

$Si + 2h^+ \rightarrow Si^{2+}$ Oxidised by HNO_3, "holes" are supplied by HNO_3

$H_2O \leftrightarrow OH^- + H^+$

- Combines with (OH)- to form the hydroxide: $Si^{2+} + 2OH^- \rightarrow Si(OH)_2$
- Subsequently liberates hydrogen to form SiO_2: $Si(OH)_2 \rightarrow SiO_2 + H_2$
- Hydrofluoric acid (HF) is used to dissolve SiO_2: $SiO_2 + 6HF \rightarrow H_2SiF_6 + H_2O$

  where H_2SiF_6 is soluble in water
- The holes required for the initial oxidation is given by: $HNO_2 + HNO_3 \rightarrow 2NO_2^- + 2h^+ + H_2O$

  $2NO_2^- + 2H^+ \rightarrow 2HNO_2$

The overall reaction is: $Si + HNO_3 + 6HF \rightarrow H_2SiF_6 + HNO_2 + H_2O + H_2$

The by-products after etching are typically gaseous or water soluble for ease of removal.

Practice Question 2 – Buffered HF

The overall reaction of the Si etching is shown:

$$Si + HNO_3 + 6HF \rightarrow H_2SiF_6 + HNO_2 + H_2O + H_2$$

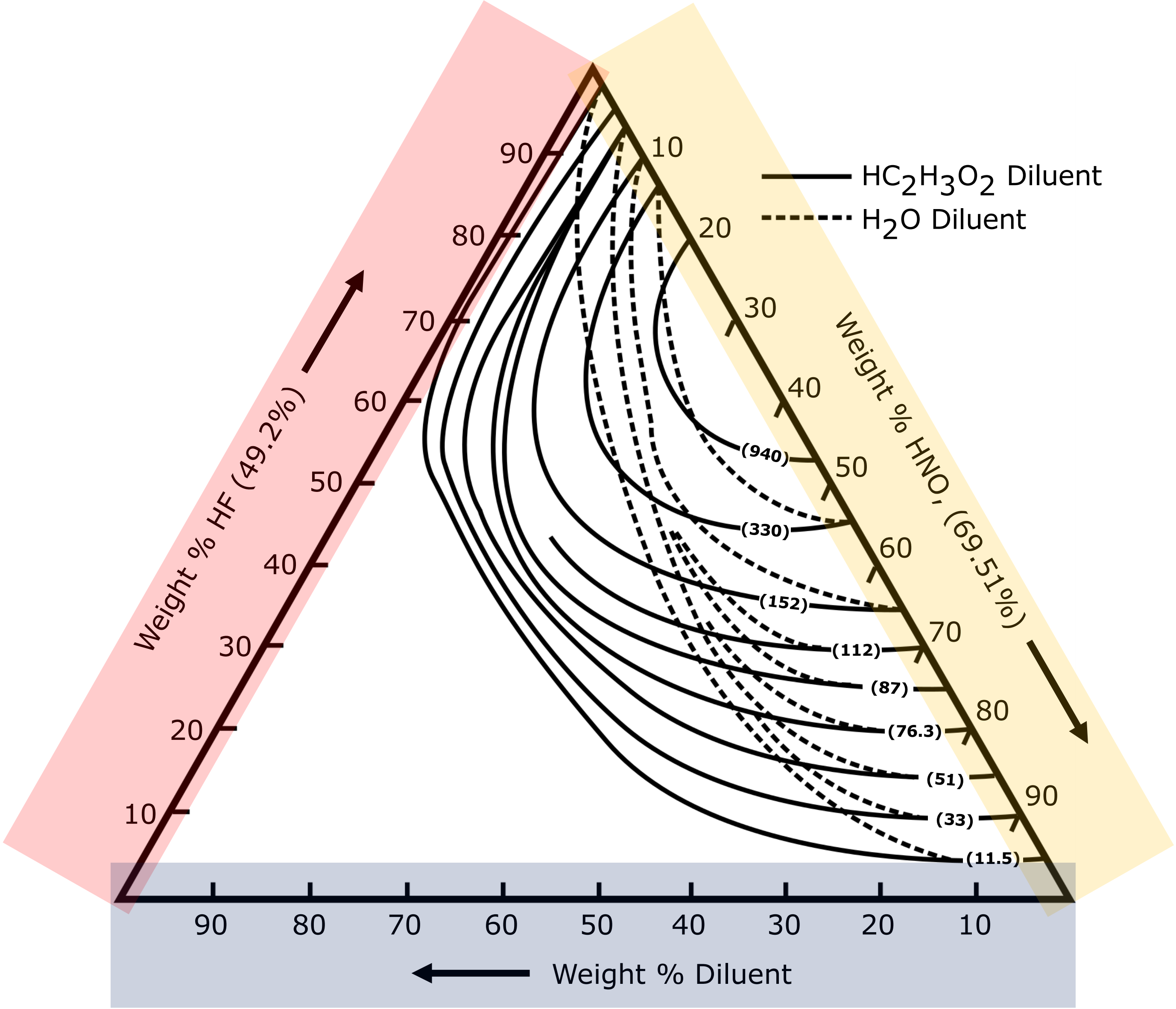
From the overall reaction, explain why the etch rate will decrease with time.

Pause and try out this question

Solution:

- In regular Si etching, SiO_2 etching reaction consumes HF and causes the reaction rate of SiO_2 etching to decrease.
- Buffered HF (NH_4F) is used to provide consistent etch rate by maintain HF concentration. $NH_4F \rightarrow NH_3\uparrow + HF$

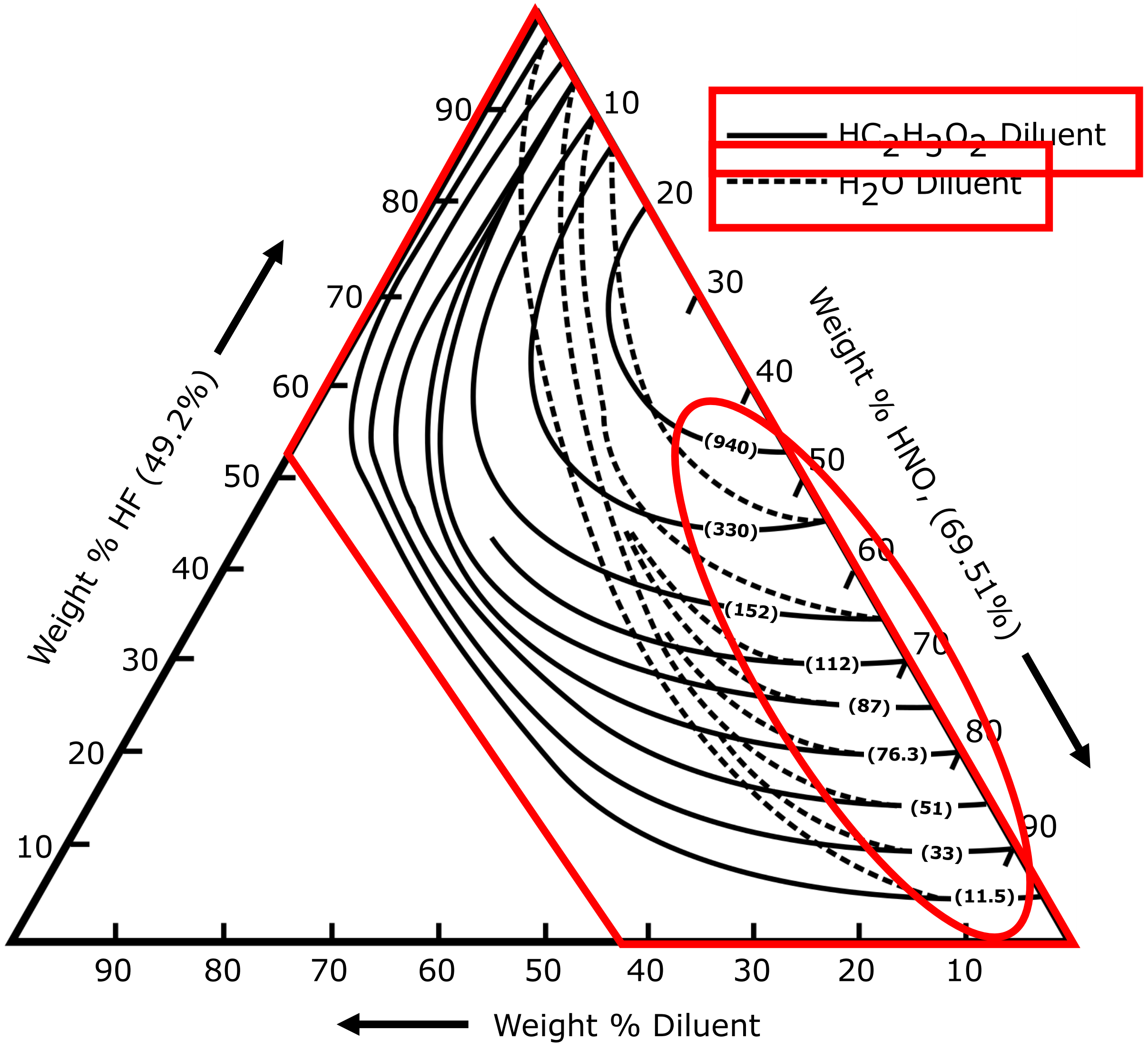
Introduction to Iso-Etch Curve



The silicon etch rate is determined under different concentrations of HNO_3, HF and diluent:

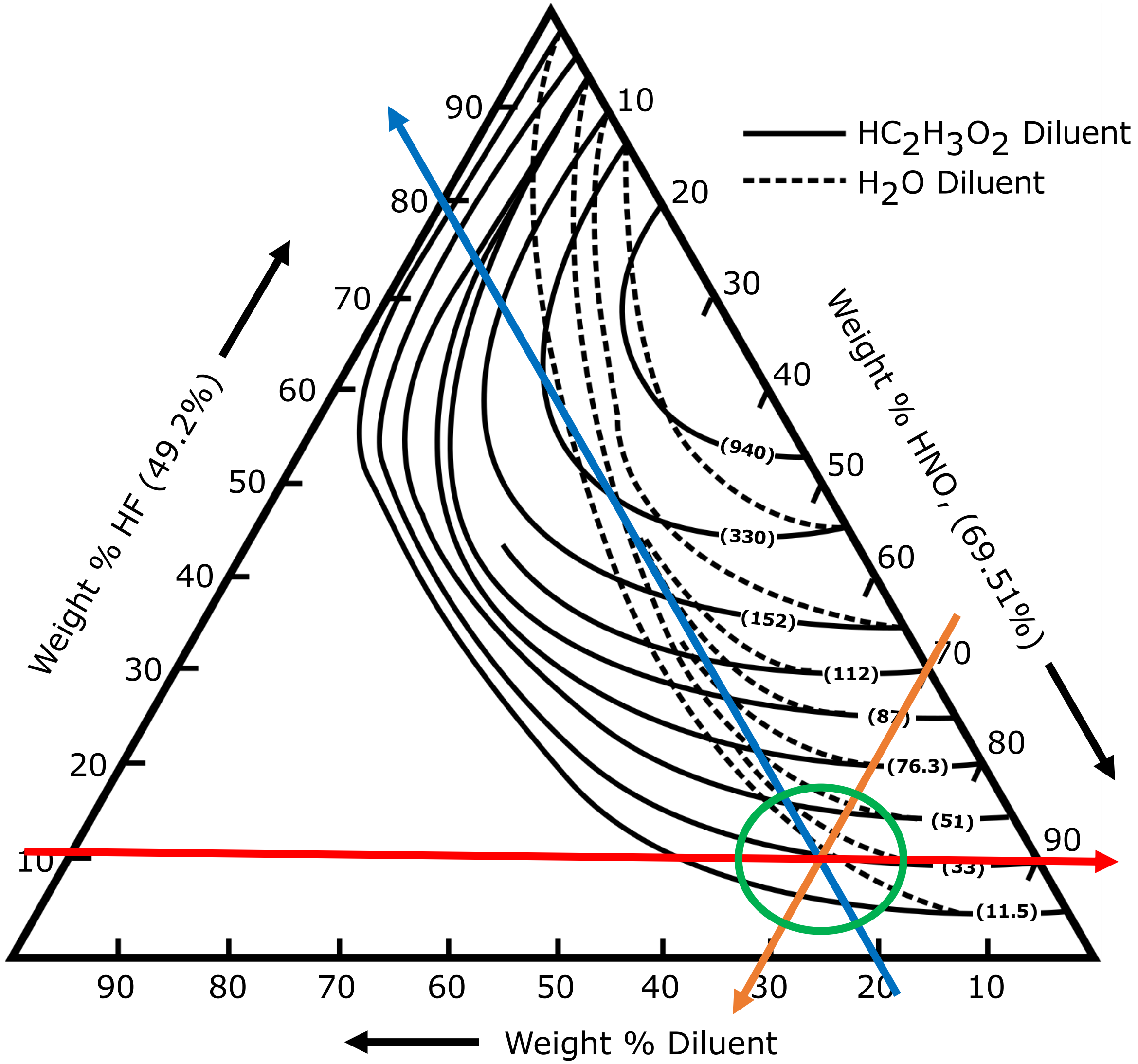
- **Concentration of HF**
- **Concentration of NHO_3**
- **Concentration of diluent. The diluent is usually water or acetic acid**

Introduction to Iso-Etch Curve



- The contour lines indicate the etch rate of Si at specific concentrations.
- The numbers in the bracket indicate the Si etch rates in μm/min.
- The solid lines indicate the etch rates when acetic acid diluent is used.
- The dash lines indicate the etch rates when water diluent is used.

Determining the Si Etch Rate From Iso-Etch Curve



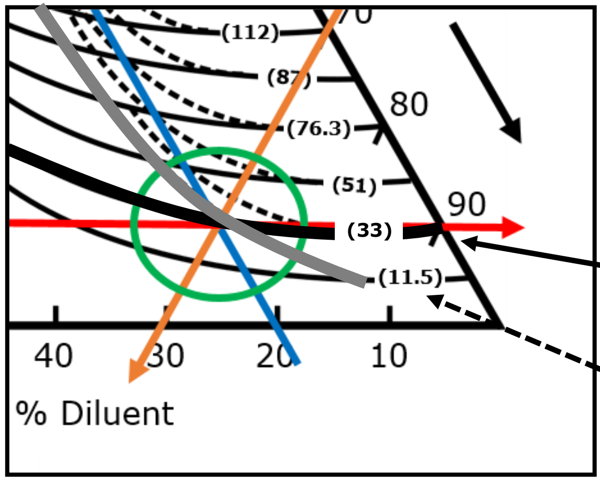
How to determine the Si etch rate using the Iso-etch curve?

For example, if a mixture of 10% HF, 70% HNO_3, and 20% water diluent is used as Si etchant:

1. Draw a line of such from 10% HF axis
2. Draw a line of such from 70% HNO_3 axis
3. Draw a line of such from 20% diluent axis
4. Intersection point of these three lines falls at 11.5 μm/min curve of the dash line (water diluent). Therefore, the Si etch rate is 11.5 μm/min

Pause and observe carefully

Water vs Acetic Acid as Diluent

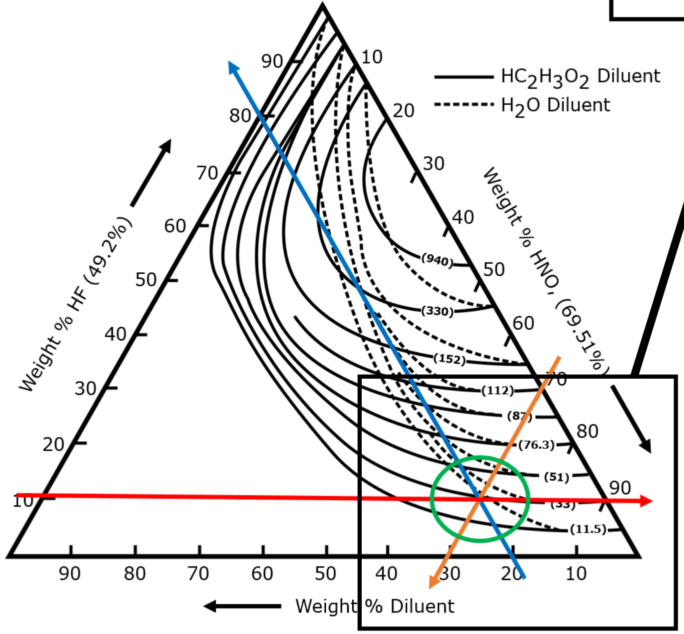


33 µm/min if acetic acid is used

10% HF, 70% HNO_3, 20% CH_3COOH

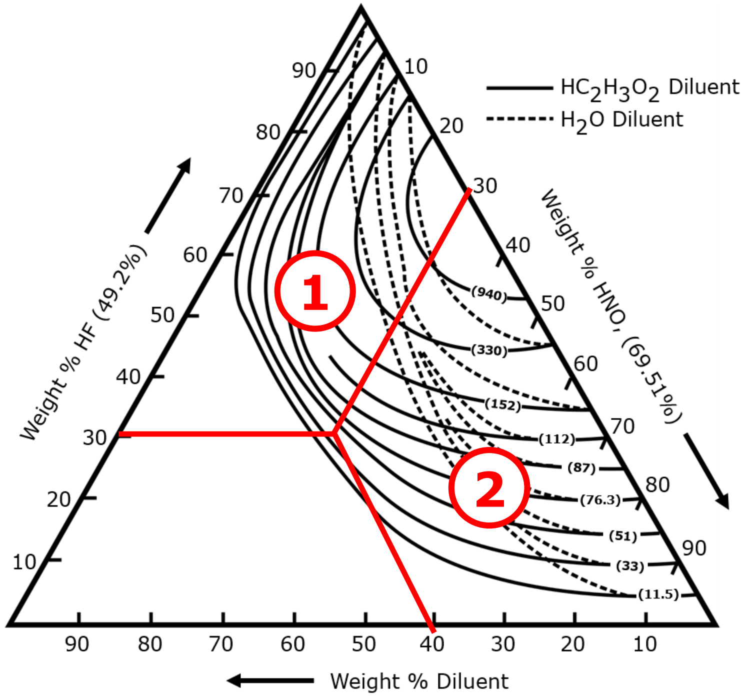
11.5 µm/min if water is used

10% HF, 70% HNO_3, 20% H_2O



- Acetic acid (CH_3COOH) is frequently substituted for water as the diluent.
- It has a lower dielectric constant than water.
- It also produces less dissociation of the HNO_3, and yields a higher oxidation power for the etching process.

Iso-Etch Curve for Silicon



HNO_3 oxidises Si to form SiO_2

HF etch away the SiO_2

Region 1:

High HF concentrations, low HNO_3 concentration, insufficient HNO_3 to oxidise the Si for HF to etch

- Reaction limited by HNO_3
- The HNO_3 concentration controls the etch rate
- Etch rate is limited by oxidation, less oxide is formed on Si

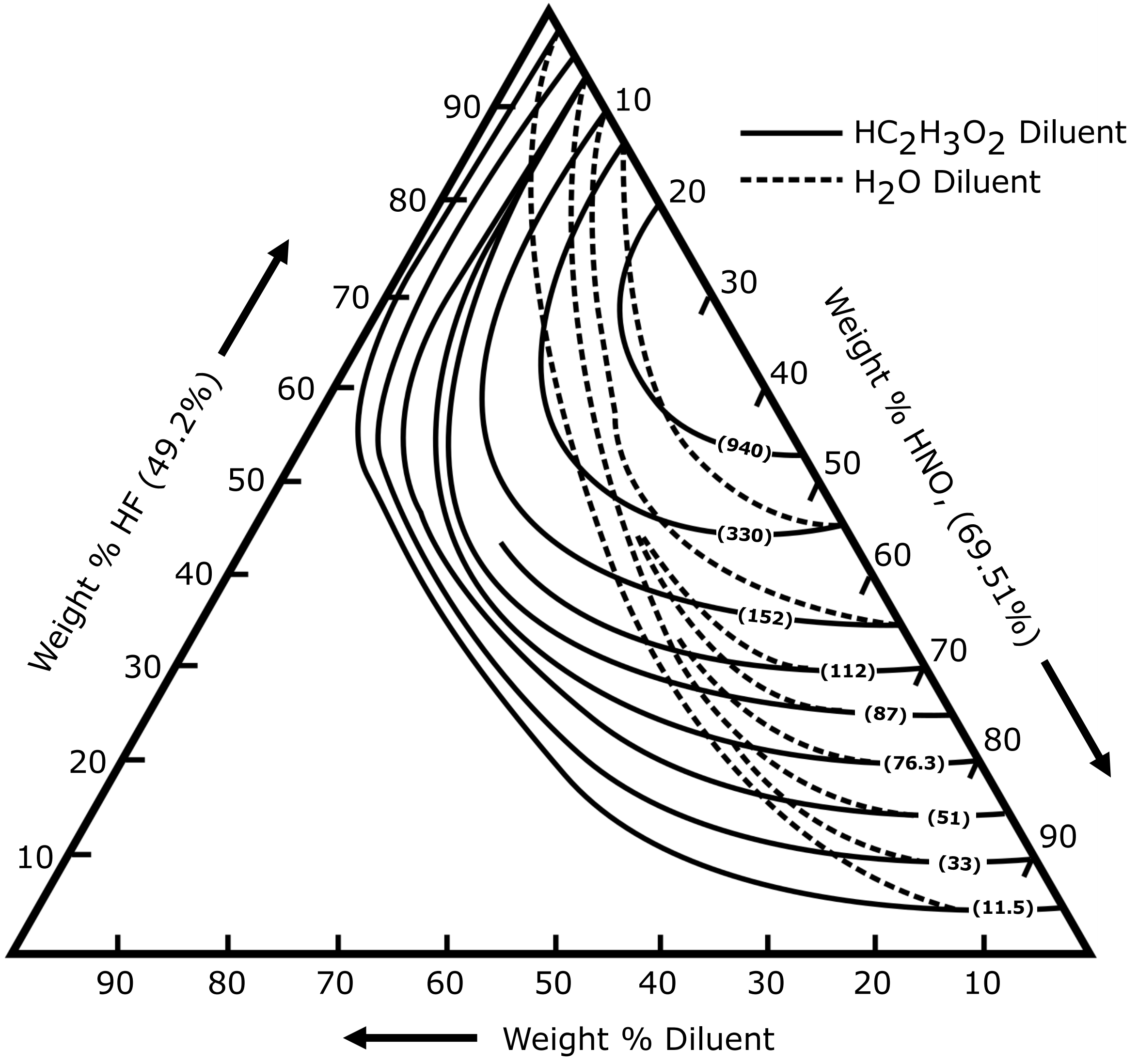
Region 2:

High HNO_3 concentrations, low HF concentration, insufficient HF to etch away the silicon oxide formed by HNO_3

- Reaction limited by HF
- Ability of HF to remove the SiO_2 controls the etch rate
- Etch rate limited by reduction, more oxide is formed on Si

Pause and observe carefully

Practice Question 3



A mixture of 75% HF, 20% HNO_3, and 5% H_2O is used as an etchant for Si.

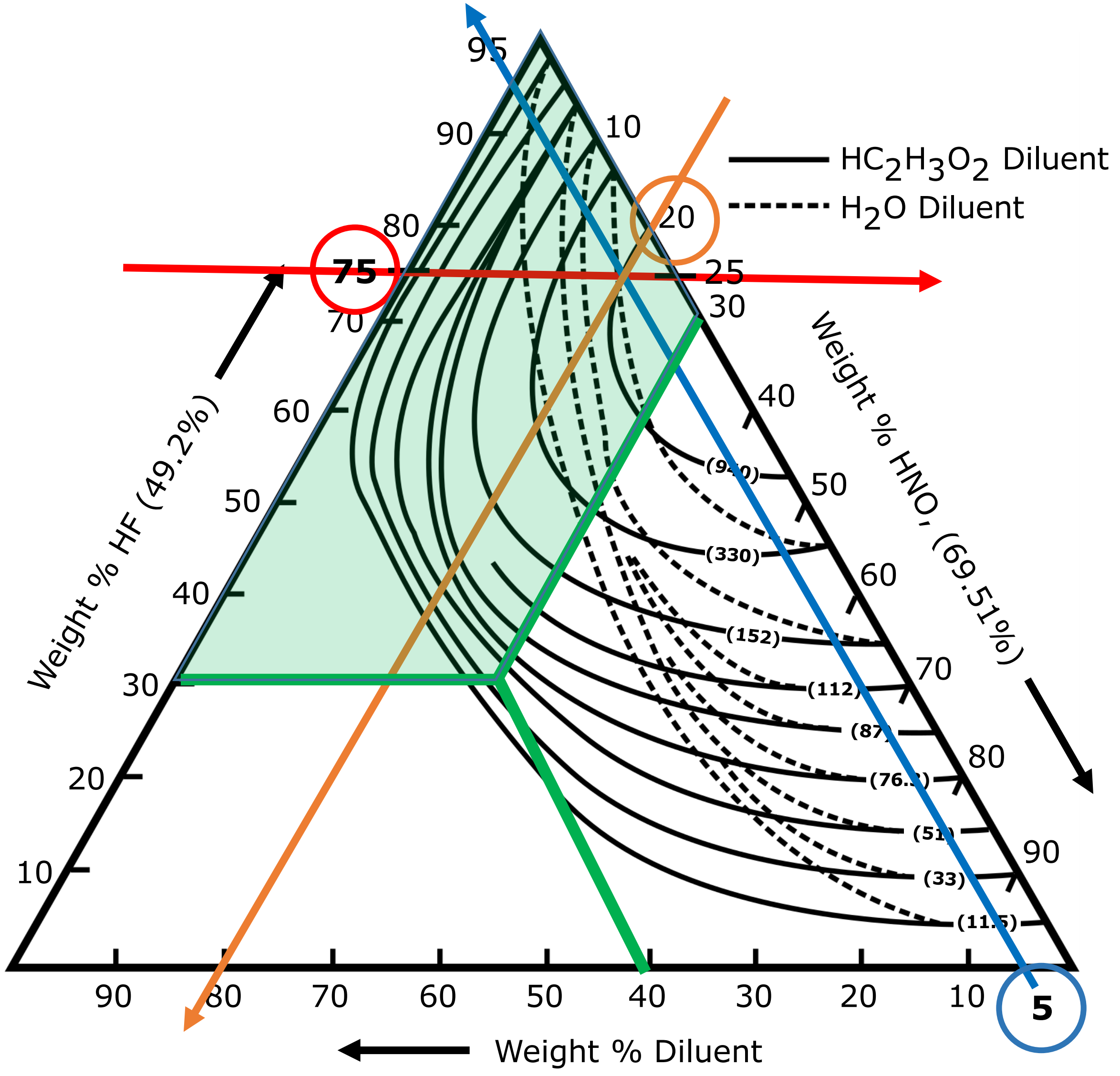
a) What is the etch rate?

b) Which is the possible limiting factor for this etchant? (HF or HNO_3 concentration?)

c) 5% water in the mixture is replaced with acetic acid as the diluent. What is the new etch rate?

Pause and try out this question

Practice Question 3



A mixture of $\boxed{75\%\ HF,}$ $\boxed{20\%\ HNO_3,}$ and $\boxed{5\%\ H_2O}$ is used as an etchant for Si.

a) What is the etch rate?

The etch rate is 330 µm/min.

b) What is the possible limiting factor of this etchant? (HF or HNO_3 concentration?)

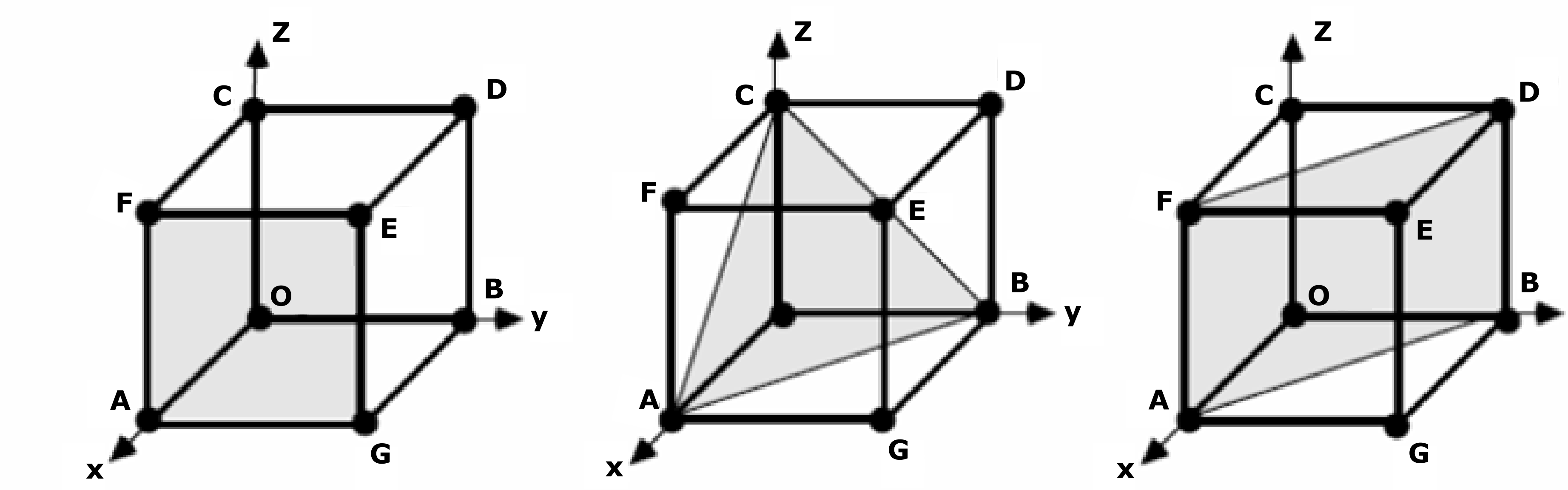
The reaction is limited by HNO_3 concentration, which corresponds to oxidation rate of the Si.

c) 5% water in the mixture is replaced with acetic acid as the diluent. What is the new etch rate?

The new etch rate is 940 µm/min.

Orientation Dependent Etching

Silicon Wafer Crystal Orientation



(100) (111) (110)

Different Si atomic planes have different etch rates in KOH etchant.

Orientation Dependent Etching

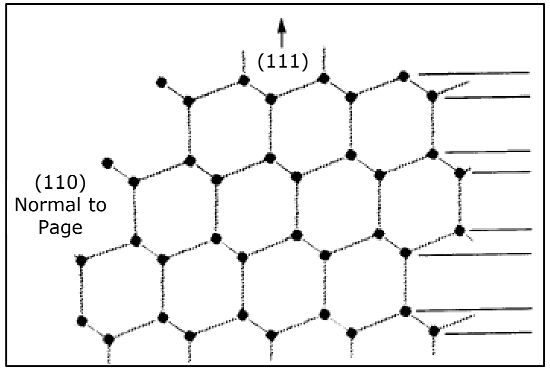
Some etchants dissolve a given crystal plane of a semiconductor faster than other planes.

Example: KOH in water and isopropyl alcohol.

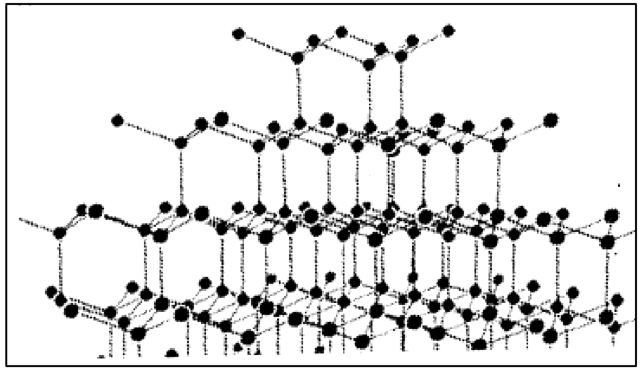
Etching rate for Si: 0.6μm/min for (100) plane

0.1μm/min for (110) plane

0.006μm/min for (111) plane



(110)



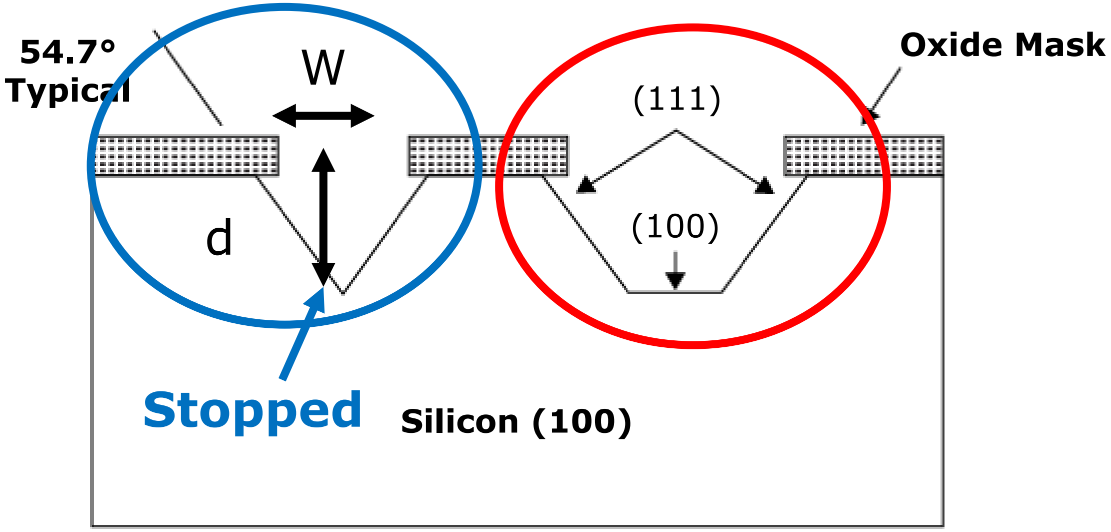
(111)

- Si (111) plane is closely packed → Slowest etching
- (111) plane of Si oxidises faster than other planes, thus the surface is covered faster with oxide, which blocks further dissolution

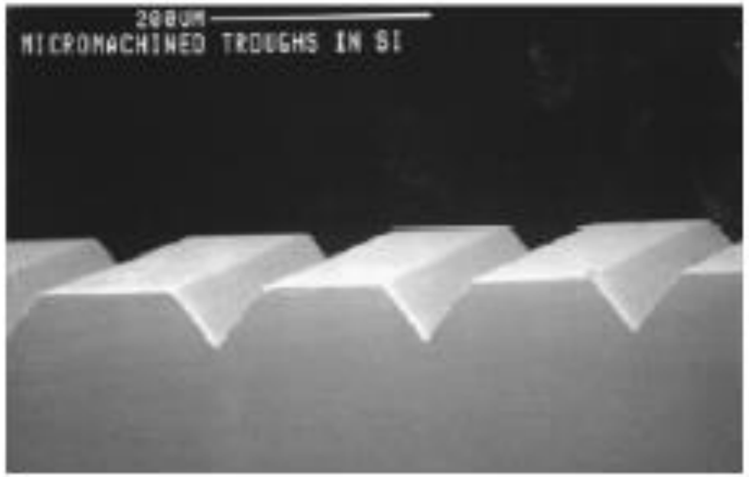
Orientation Dependent Etching (Cont'd.)

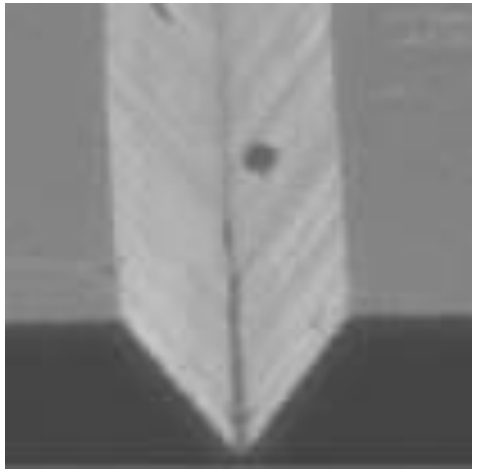
- Through an oxide mask, KOH etching of Si forms (111) planes at the side walls
- Since (111) has a slow etch rate, it forms a self-stopping V-groove. (111) plane makes an angle of 54.7° with (100) naturally, the width (W) of the defined image approximately determines the depth (d) following the relation:

$$d \approx \frac{W}{2} \tan 54.7 \approx 0.7\,W$$



V-Shaped Groove Formation in the (100) Silicon with Anisotropic Etching





Practice Question 4

Compare the etching characteristics of (100) and (111)-oriented silicon wafers. Give at least two applications of orientation dependent etching.

Pause and try out this question

Some etchants dissolve a given crystal plane of a semiconductor faster than other planes. Etching speed changes from one crystal plane to another crystal plane when they are in a different orientation group. Especially (111) phase of Si has more atoms per unit area compared to (100) plane, thus making more difficult to etch (111) plane than the (100) plane, therefore slower etching rate on the (111) plane.

Applications of orientation dependent etching:

- Chemical machining of semiconductor materials
- V shaped and vertical groove cutting
- Wafer defect investigation (crystal defects)

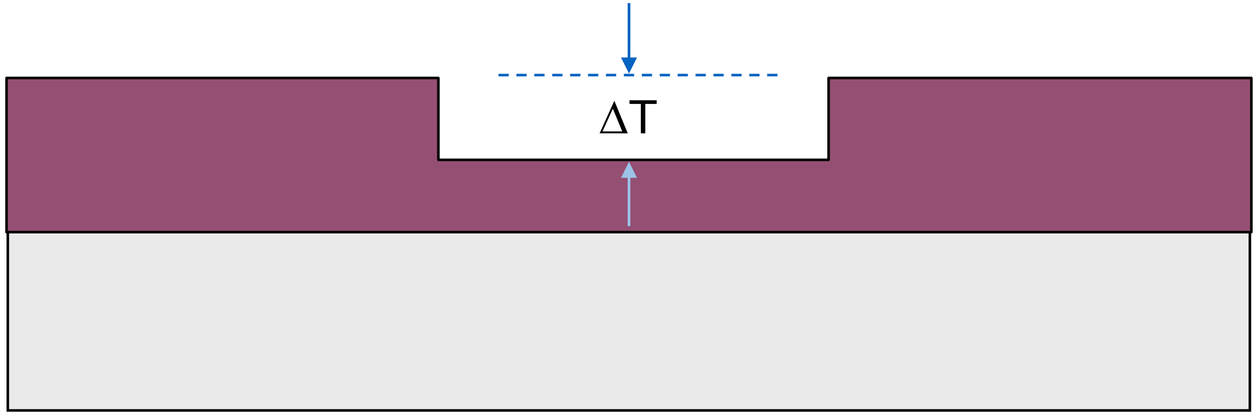
Etch Parameters

Some Etch Parameters

- Etch rate
- Undercut and over-etch
- Selectivity

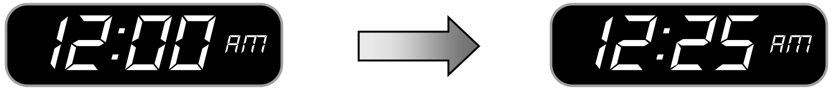
Etch Rate

ΔT = Change in Thickness



$$\text{Etch Rate} = \frac{\Delta T}{t}$$

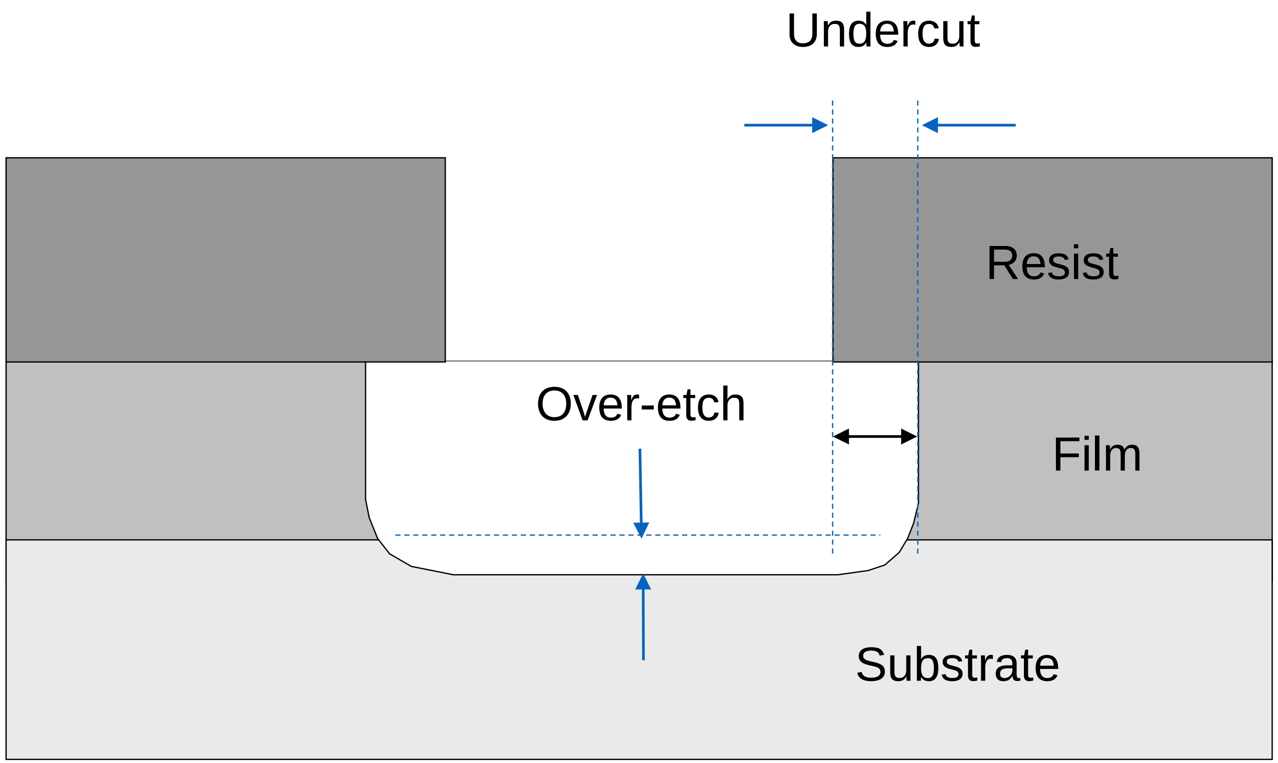
t = Elapsed Time during Etch



Start of Etch

End of Etch

Etching Undercut and Overetch



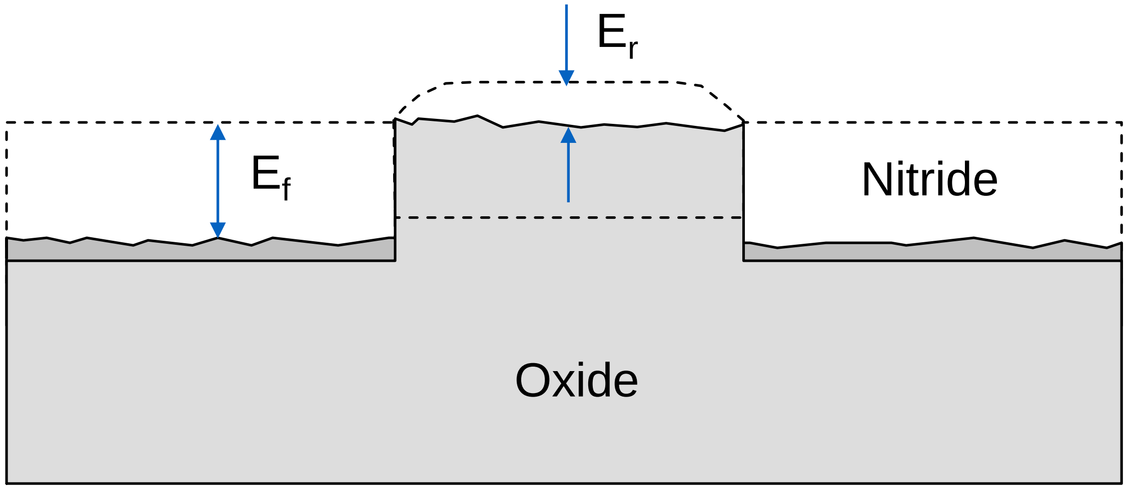
Etch Selectivity

Selectivity is the ratio of the etch rates between the different materials, especially the material that needs to be etched as compared to the material that we do not want to remove.

(E_f: high etch rate; E_r: low etch rate)

$$S = \frac{E_f}{E_r}$$

HIGH SELECTIVITY MEANS THAT ETCHING ONLY OCCURS ON THE DESIRED LAYER!



Etch Selectivity (Cont'd.)

What affects selectivity?

- **Impurity type and/ or concentration**
- **Material composition**

Examples:

Impurity concentration:

Etchant:
KOH:water:isopropyl alcohol of 7:19:4

Etch Rates:
- **0.94 µm/cm^{-3}** n/p-doped Si of **10^{14} to 10^{18} cm^{-3}**
- **0.02 µm/cm^{-3}** n/p-doped Si of **10^{18} to 10^{20} cm^{-3}**

Application:
Highly doped n/p layer inserted intentionally as etch stop.

Material composition:

Etchant:
Nitric Acid:H_2O_2 of 10:1

Selectivity:
In GaAs/ AlGaAs compound, the etch selectivity in removing GaAs is 95.

Application:
Often used in GaAs technology.

Practice Question 1

0.6μm of SiO_2 is to be etched; the rate is 0.2 μm/min.

If etch selectivity of the oxide relative to **mask** is 24:1, the SiO_2 is slightly over-etched for 3.6 minutes. **What is the minimum thickness of the mask**?

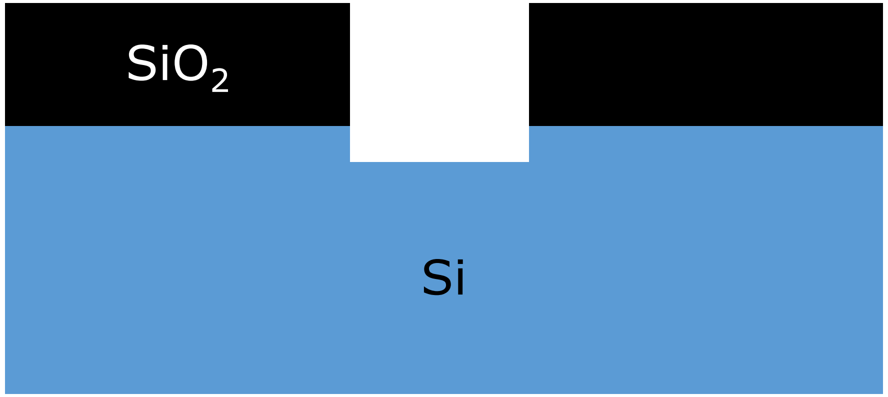
Pause and try out this question

Solution:

$$S = \frac{r_{oxide}}{r_{mask}} = \frac{24}{1} = \frac{0.2\mu m/min}{Thickness/3.6min}$$

$$\text{Mask thickness} = \frac{0.2 \text{ x } 3.6}{24} = 0.03$$

Mask should be at least 0.03μm thick.



How thick is a 0.035μm mask after 3.6 minutes of etching?

$$t_{mask}(3.6) = 0.035 \text{ μm} - \boxed{\frac{0.2}{24}} \text{ x } \boxed{3.6} = 5 \text{ nm}$$

Etch Rate of Mask   Etch Time

Lesson Summary - Etching

Comparison:

- Wet etching usually yields isotropic etching profile; whereas dry etching usually yields anisotropic etching profile.
- Wet etching uses wet chemical etchant; whereas dry etching uses ionic/ plasma etchant.

Wet Etching:

- Wet etching uses chemical etchants to etch away the target materials.
- In wet etching of Si, HNO_3 is used to oxidise Si into SiO_2; and HF is used to etch away the formed SiO_2.
- The etching rate of Si depends on its crystal orientation for certain etchants.

Practice Question 2

Determine if the statements below are true or false.

Pause and try out this question

a) Isotropic etches at the same rate in all directions (for A = 0) True

b) Anisotropic etch is more likely to cause underetching False

c) Wet chemical etching normally produces isotropic profiles True

d) Anisotropic etches in only one direction (for A = 1) True

e) Anisotropic etches perpendicular to the wafer surface True

f) Low lateral etching is a characteristic of isotropic etch False

g) Vertical sidewalls are a characteristic of isotropic etch False

h) Higher packing density in ULSI chips is achievable due to anisotropic etch characteristics True

Practice Question 3

Define etch selectivity. Does wet etching have good or poor selectivity? What does high selectivity mean? State and explain the selectivity formula.

Pause and try out this question

Selectivity represents how much faster one film etches than another film under the same etch conditions. It is the ratio of the etch rates between the different materials, especially the material that needs to be etched compared with the material that we do not want to remove.

Wet etching has good selectivity. High selectivity means that etching only occurs on the desired layer.

$$S = \frac{E_f}{E_r}$$

(E_f: High etch rate; E_r: Low etch rate)