

FC250 Nano- and microtechnologies

chapter 4. Basic Microfabrication Techniques - Etching

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Outline - chapter 4. Basic Microfabrication Techniques - Etching

- 4.1 Lithography

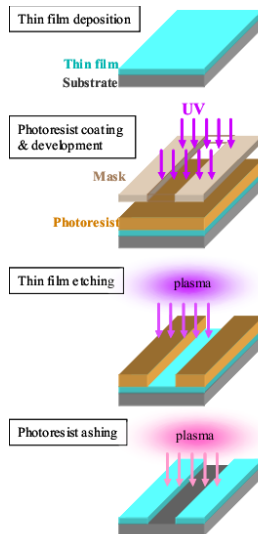
- 4.2 Etching and Substrate Removal
 - 4.2.1 Wet Etching
 - 4.2.2 Dry Etching

4.1 Lithography

Lithography - process flow

Microlithography is a technique that creates microstructures after given geometrical template:

- ▶ Lithography is usually applied to shape a thin film
⇒ deposition of thin film
- ▶ Photosensitive material (resist) is coated on the material that should be shaped
- ▶ Resist is irradiated through a mask, by projection of UV image or by directed electrons (photolithography or electron lithography)
- ▶ Resist development:
 - ▶ positive resist: soluble in developer at the irradiated places
 - ▶ negative resists: insoluble in developer at the irradiated places
- ▶ Etching of the film through photoresist pattern
- ▶ Rest of the resist is removed



lithography patterning with positive resist

Photolithography - step details

- ▶ creation of the mask layout on a computer
- ▶ generation of a photomask
a sequence of photographic processes (using optical or e-beam pattern generators) that results in a glass plate that exhibits the desired pattern in the form of a thin (≈ 100 nm) chromium layer.
- ▶ deposition of thin film (discussed later)
- ▶ spin-coating of a photoresist (positive or negative)
polymeric photosensitive material spun onto the wafer in liquid form (an adhesion promoter such as hexamethyldisilazane, HMDS, is usually used prior to the application of the resist). The spin speed and photoresist viscosity determine the final resist thickness, which is typically between 0.5 – 2.5 μm . Due to the better process control that can be achieved for small geometries, the positive resist is most commonly used in VLSI processes.
- ▶ soft-baking (5 – 30 min at 60 – 100 $^{\circ}\text{C}$) in order to remove the solvents from the resist and to improve the adhesion.
- ▶ mask alignment to the wafer
- ▶ exposure of photoresist to a UV source - photoresist is developed in a process similar to the development of photographic films
- ▶ hard baking of the resist (improvement of adhesion)
 20 – 30 min at 120 – 180 $^{\circ}\text{C}$
- ▶ etching of underlying thin film through created pattern on wafer
- ▶ removal of the photoresist in acetone or another organic removal solvent

Techniques for Photolithography

Three different exposure systems (depending on the separation between the mask and the wafer):

1. contact - better resolution than the proximity technique **but constant contact of the mask with the photoresist reduces the process yield and can damage the mask**
2. proximity
3. projection - uses a dual-lens optical system to project the mask image onto the wafer
⇒ one die exposed at a time ⇒ step and repeat system to completely cover the wafer area. **The most popular microfabrication system yielding superior resolutions to the contact and proximity methods.**

The exposure sources used for photolithography depends on the resolution.

- ▶ above $0.25\ \mu\text{m}$ minimum line width ⇒ high-pressure mercury lamp (436 nm g-line and 365 nm i-line),
- ▶ between 0.25 and $0.13\ \mu\text{m}$ ⇒ deep UV sources such as excimer lasers (248 nm KrF and 193 nm ArF),
- ▶ below $0.13\ \mu\text{m}$ regime ⇒ extensive competition between e-beam, X-ray and extreme UV (EUV) (with a wavelength of 10–14 nm)

4.2 Etching and Substrate Removal

Classification of Etching/Sputtering Processes

Basic classification:

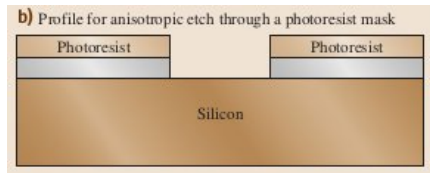
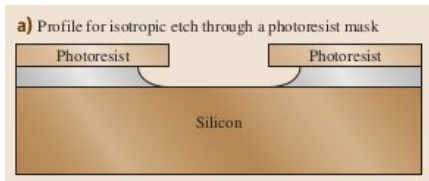
- ▶ wet etching
- ▶ dry etching

Classification according to the type of process:

- ▶ ion sputtering
- ▶ chemical etching
- ▶ plasma etching

Two important properties of etching:

- ▶ selectivity - degree to which the etchant can differentiate between the layer to be etched and the masking layer or underlying material
- ▶ directionality - isotropic versus anisotropic etching



Properties of Etching/Sputtering Processes

ion sputtering

- ▶ purely physical approach, removal by energy transfer
- ▶ slow process, no selectivity
- ▶ ions are directed by electric field, i.e. anisotropic process

chemical etching

- ▶ purely chemical processes that requires aggressive chemicals and/or elevated temperature for reaction activation
- ▶ can be very fast, selective
- ▶ chemical reactions with surface are not directed, i.e. isotropic process

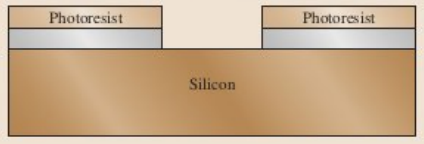
plasma etching

- ▶ combination of physical and chemical approaches
- ▶ directional process

a) Profile for isotropic etch through a photoresist mask



b) Profile for anisotropic etch through a photoresist mask



4.2.1 Wet Chemical Etching

- ▶ isotropic process (except for crystalline materials) \Rightarrow lateral undercut, minimum feature size $> 3 \mu\text{m}$
- ▶ superior selectivity to the masking layer as compared to dry techniques

Historically, wet etching techniques preceded the dry ones. Still important for micro/nanofabrication in spite of their less frequent utilization in VLSI technology.

Etching of SiO_2

- ▶ etchant - dilute (6:1, 10:1 or 20:1 by volume) or buffered HF (BHF: $\text{HF} + \text{NH}_4\text{F}$) solutions
- ▶ masking materials - photoresist or silicon nitride
- ▶ etch rate $\approx 100 \text{ nm/min}$ in BHF

Etching of Si_3N_4

- ▶ phosphoric acid $(\text{H}_3\text{PO}_4)_4$ at $140\text{--}200^\circ\text{C}$
- ▶ masking materials - silicon oxide
- ▶ not commonly used due to the masking difficulty and nonrepeatable etch rates

Etching of metals - Al, Cr, Au various etchants combining acid and base solutions, commercially available

Wet Chemical Etching

Anisotropic and isotropic wet etching of crystalline (Si and GaAs) and amorphous (glass) substrates is an important topic in micro/nanofabrication. The realization of anisotropic wet etching of c-Si is considered to mark the beginning of micromachining and MEMS fabrication.

Isotropic etching of c-Si

- ▶ HF/HNO₃/CH₃COOH etchant - "HNA" stands for hydrofluoric acid (HF), nitric acid (HNO₃) and acetic acid (CH₃COOH). HNO₃ oxidizes Si, HF dissolves the oxide, CH₃COOH prevents the dissociation of HNO₃
- ▶ masking materials - SiO₂ for short etch time otherwise Si₃N₄
- ▶ dopant selectivity - etch rate drops at lower doping concentrations ($< 10^{17} \text{ cm}^{-3}$ n- or p-type), it can be as etch-stop mechanism but it is not widespread due to its difficulty

Isotropic etching of glass

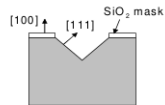
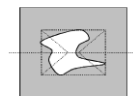
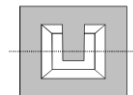
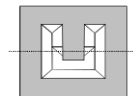
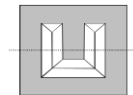
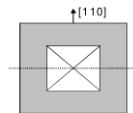
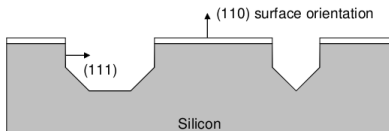
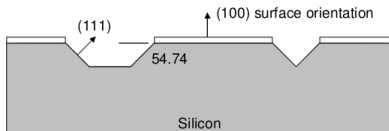
- ▶ etchant - HF/HNO₃
- ▶ masking materials - Cr/Au for shorter time, long etching requires a more robust mask (bonded Si)
- ▶ etching results in rough surfaces, used in fabrication of microfluidic components (mainly channels)

Wet Chemical Etching

Anisotropic etching of c-Si

- ▶ three possible anisotropic etchants attacking c-Si along preferred crystallographic directions:
 - ▶ potassium hydroxide (KOH),
 - ▶ ethylenediamine pyrocatechol (EDP - a typical formulation consists of ethylenediamine $\text{NH}_2\text{-CH}_2\text{-CH}_2\text{-NH}_2$, pyrocatechol $\text{C}_6\text{H}_4(\text{OH})_2$, pyrazine $\text{C}_4\text{H}_4\text{N}_2$ and water)
 - ▶ tetramethyl ammonium hydroxide (TMAH)
- ▶ etch rate $\approx 1 \mu\text{m}/\text{min}$ at temperature 85–115 °C
- ▶ etch rate slowest for (111) planes \Rightarrow used to create beams, membranes and other mechanical and structural components, markedly reduced in heavily ($> 5 \times 10^{19} \text{ cm}^{-3}$) boron-doped (p^{++}) regions
- ▶ etching chemistry is not quite clear: Si oxidation at surface and reaction with hydroxyl ions (OH^-) creates soluble silicon complex ($\text{SiO}_2\text{OH}^{2-}$)
- ▶ masking materials - SiO_2 and Si_3N_4 (superior for longer etch times)

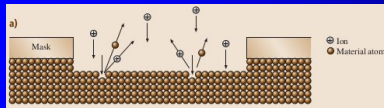
Examples of Si Anisotropic Etching



4.2.2 Dry Etching

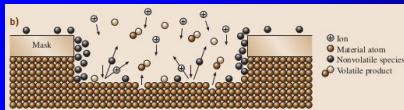
Types of Directional Dry Etching

ion sputtering (milling)



- pressure 0.01 – 0.1 Pa, Ar⁺
- etch rate few nm/min
- poor selectivity (close to 1:1 for most materials)

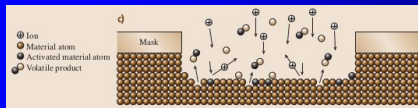
high-pressure plasma etching



- pressure 15 – 500 Pa
- highly reactive plasma species produce volatile molecules
- nonvolatile species are removed by low-energy ions

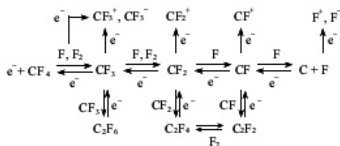
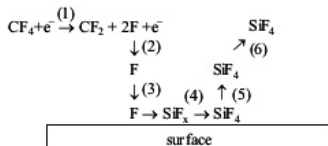
→ directional etching due to passivation of side walls by nonvolatile species

reactive ion etching (RIE)

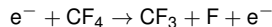


- pressure 1 – 10 Pa
- reactive species react only with activated atoms of material, activation achieved by the collision with an incident ion

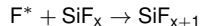
Principles of Plasma Etching – Plasma Chemistry



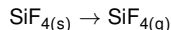
1. Creation of reactive species within plasma phase by electron–neutral collisions



2. Transport of reactive species from plasma to substrate
3. Adsorption of reactive species on surface (physisorption or chemisorption)
4. Surface or volume diffusion of reactants, formation of desorbing species



5. Desorption of product species



6. Transport of product species into plasma
7. Simultaneous re-deposition of etching products

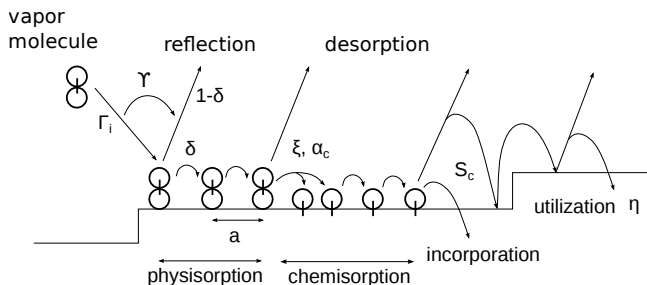
Adsorption

Consider a molecule approaching a surface from the vapor phase.

- ▶ **A few atomic distances from the surface** molecule begins to feel an attraction - interaction with the surface molecules by **van der Waals forces** (London dispersion forces):
 - ▶ molecules/atoms without dipole moments (symmetrical or inert) interact due to oscillating dipoles, i.e. induced-dipole interaction
 - ▶ polar molecules (permanent dipoles) interact more strongly
- ▶ The approaching molecule is **being attracted into a potential well** - accelerates down the curve until it passes the bottom and is **repelled by steeply rising potential**.

Physisorption

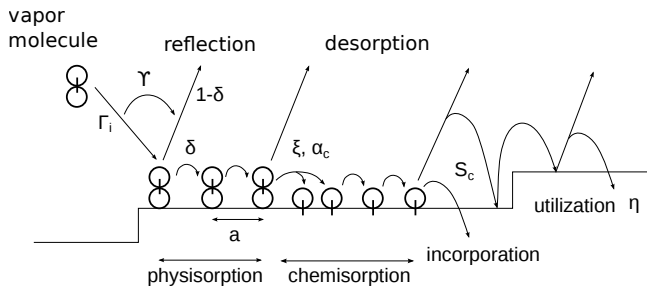
- ▶ If enough of the molecule's perpendicular component of momentum is dissipated into the surface the molecule cannot escape the well after being repelled \Rightarrow **physisorption**
 - ▶ fraction of physisorbed molecules - **trapping probability δ**
 - ▶ reflected $1 - \delta$
 - ▶ δ is different from **thermal accommodation coefficient γ** introduced previously, molecule is at least partially accommodated thermally to the surface temperature T_s even when it is reflected
- ▶ The physisorbed molecule is mobile on the surface except at cryogenic T - **hopping (diffusing)** between surface atomic sites.



Chemisorption

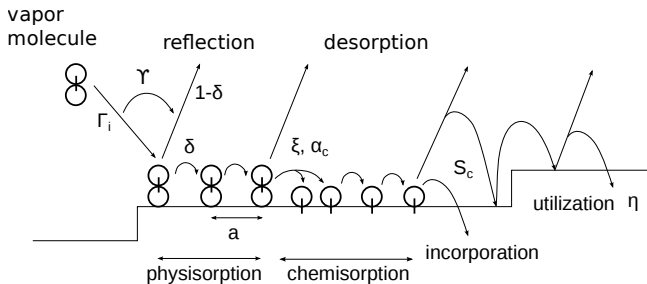
During surface diffusion the molecule

- ▶ may **desorb** after a while by gaining enough energy in the tail of the thermal energy distribution.
- ▶ may undergo a further interaction consisting of the formation of chemical bonds with the surface atoms, i. e. **chemisorption**. The **chemisorption reaction probability** ξ is used in the case of chemisorption on a foreign substrate instead of **condensation coefficient** α_c .
- ▶ some of adsorbed species eventually escape back into the vapor phase \Rightarrow **sticking coefficient** S_c - fraction of the arriving vapor that remains adsorbed for the duration of the experiment.



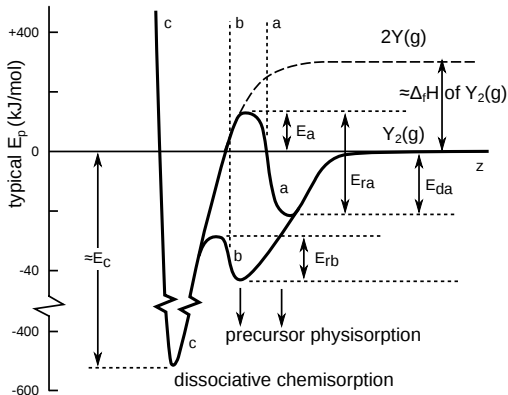
Chemisorption

- ▶ **Sticking coefficient** S_c has less fundamental meaning than δ and ξ (or α_c) that are determined solely by chemistry and energy. Nevertheless, S_c is very useful in thin film deposition - it is the fraction of arriving vapor incorporated into the film (buried before escaping).
- ▶ **Utilization fraction** η of a chemical vapor - fraction of molecules utilized for the deposition $\Rightarrow \eta$ can approach unity even when S_c is very low.



Energetics of Precursor Adsorption Model

Consider hypothetical diatomic gas-phase molecules $Y_2(g)$ adsorbing and then dissociative chemisorbing as two Y atoms:



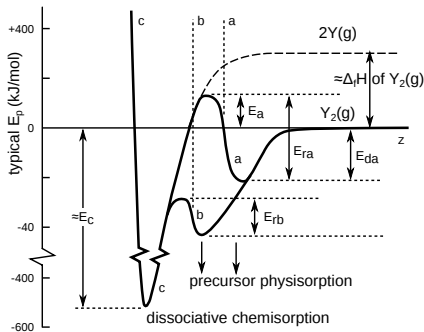
Lifting **atomic Y** out of its potential well along **curve c** results in much higher molar potential energy E_p in the gas phase - roughly the **heat of formation, $\Delta_f H$** , of $2Y(g)$ from $Y_2(g)$.

The **curve a** represents **activated chemisorption** - there is an activation energy E_a to be overcome for $Y_2(g)$ to become dissociatively chemisorbed.

For deeper precursor well, **curve b**, chemisorption is not activated though there is still a barrier E_{rb} .

Eley-Rideal and Langmuir-Hinshelwood mechanisms

- ▶ If **curve c** is followed (E_p is high enough) direct chemisorption (without involving precursor state) \Rightarrow **Eley-Rideal mechanism**, i.e. direct reaction between an incoming species and a surface site
- ▶ Reaction among surface species \Rightarrow **Langmuir-Hinshelwood mechanisms**



Two ways in which vapor can arrive at surface having $E_p > 0$:

- ▶ Gaseous molecules have their E_p raised by becoming dissociated.
- ▶ Solids and liquids have it raised by evaporating.

Energy-enhanced deposition processes

provide enough energy $E_p > E_a$

- ▶ sputter deposition - arriving species have kinetic energy ~ 1000 kJ/mol and $E_p > 0$.
- ▶ plasma-enhanced deposition - vapor molecules are dissociated in plasma

Principles of Plasma Etching - Spontaneous Etching

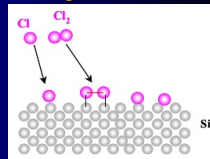
Principles of Plasma Etching – Spontaneous Etching

Neutral species from plasma interact with solid surface to form volatile products **in the absence of energetic radiation** (ion bombardment, UV radiation)

Etching rate follows **Arrhenius relationship** because it is limited by surface reaction kinetics:

$$ER_s = k_0 e^{\left(\frac{-E_a}{KT}\right)} Q$$

Q flux of reactive species, T substrate temperature, k_0 preexponential factor, E_a **activation energy**

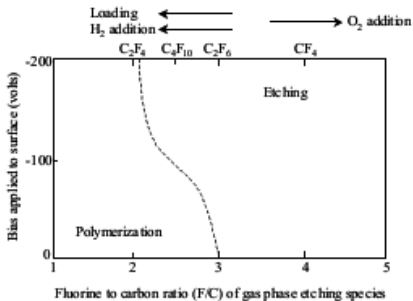


Typically, Langmuir-Hinschelwood mechanism (reaction between chemisorbed species) - creation of free radicals in plasma eliminates chemical barrier for chemisorption

Neutral	Substrate	Q (#/cm ² /s)	k_0 (Åcm ² /#min)	E_a {eV}
Cl	Poly-Si	6×10^{19}	2.57×10^{-14}	0.29
F	Si<100>	2.3×10^{19} - 1.1×10^{22}	3.59×10^{-15}	0.108

Because of higher activation energy, etching yield by atomic Cl is two orders of magnitude lower. It is consistent with high energy barrier for penetration of Cl into Si (13 eV) compared to F (1 eV)

Principles of Plasma Etching - Spontaneous Deposition



Concept of the carbon/fluorine ratio to help quantify the conditions under which polymer formation occurs.

Principles of Plasma Etching - Effect of Ions

Principles of Plasma Etching – Effect of Ions

chemical sputtering

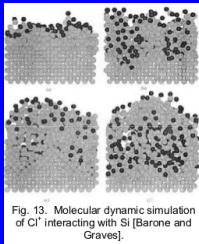
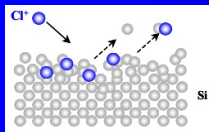
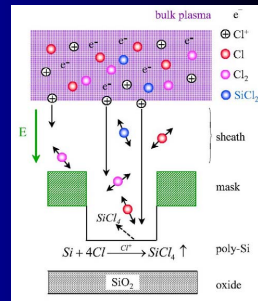
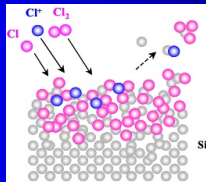


Fig. 13. Molecular dynamic simulation of Cl^+ interacting with Si [Barone and Graves].

ion-enhanced plasma etching



- highly reactive radicals , e.g. atomic chlor, created in plasma react with surface producing gaseous products
- plasma ions bombards the surface (acceleration through plasma sheath)
 - removal of surface contamination that block etching
 - contribution to etching kinetics

Types of Directional Dry Etching

Types of Directional Dry Etching

deep reactive ion etching (DRIE)

- two step cycle (see fig.)
- aspect ratio 30 : 1
- etch rate of Si = 2-3 $\mu\text{m}/\text{min}$

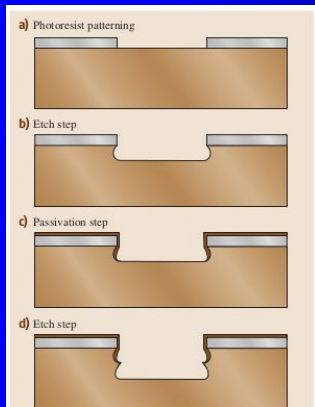


Fig. 8.17a–d DRIE cyclic process: (a) photoresist patterning, (b) etch step, (c) passivation step, and (d) etch step

Silicon DRIE:

etching step - SF_6/Ar

passivation step - $n\text{CF}_2/\text{Ar}$ (50 nm teflon-like polymer deposited on side walls)

Table 8.1 Typical dry etch chemistries

Si	CF_4/O_2 , CF_2Cl_2 , CF_3Cl , $\text{SF}_6/\text{O}_2/\text{Cl}_2$, $\text{Cl}_2/\text{H}_2/\text{C}_2\text{F}_6/\text{CCl}_4$, $\text{C}_2\text{ClF}_5/\text{O}_2$, Br_2 , SiF_4/O_2 , NF_3 , ClF_3 , CCl_4 , $\text{C}_3\text{Cl}_3\text{F}_5$, $\text{C}_2\text{ClF}_5/\text{SF}_6$, $\text{C}_2\text{F}_6/\text{CF}_3\text{Cl}$, $\text{CF}_3\text{Cl}/\text{Br}_2$
SiO_2	CF_4/H_2 , C_2F_6 , C_3F_8 , CHF_3/O_2
Si_3N_4	$\text{CF}_4/\text{O}_2/\text{H}_2$, C_2F_6 , C_3F_8 , CHF_3
Organics	O_2 , CF_4/O_2 , SF_6/O_2
Al	BCl_3 , BCl_3/Cl_2 , $\text{CCl}_4/\text{Cl}_2/\text{BCl}_3$, $\text{SiCl}_4/\text{Cl}_2$
Silicides	CF_4/O_2 , NF_3 , SF_6/Cl_2 , CF_4/Cl_2
Refractories	CF_4/O_2 , NF_3/H_2 , SF_6/O_2
GaAs	BCl_3/Ar , $\text{Cl}_2/\text{O}_2/\text{H}_2$, $\text{CCl}_2\text{F}_2/\text{O}_2/\text{Ar}/\text{He}$, H_2 , CH_4/H_2 , CClH_3/H_2
InP	CH_4/H_2 , $\text{C}_2\text{H}_6/\text{H}_2$, Cl_2/Ar
Au	$\text{C}_2\text{Cl}_2\text{F}_4$, Cl_2 , CClF_3

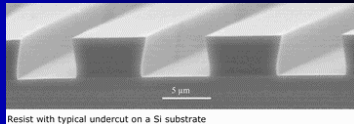
Pros and Cons of Plasma Etching

Pros and Cons of Plasma Etching

Most of dry etching applications are plasma based.



more anisotropic than chemical etching (smaller undercuts allow smaller lines to be patterned, etching of high-aspect-ratio vertical structures)



higher etch rate due to synergy of chemical etching and ion bombardment



lower etching selectivity

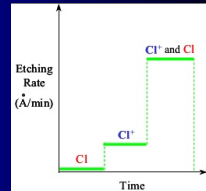


Fig. 22. Ion-enhanced etching increased the etching rate by order(s) of magnitude.