

CHAPTER 6: Etching

Different etching processes are selected depending upon the particular material to be removed. As shown in [Figure 6.1](#), wet chemical processes result in isotropic etching where both the vertical and lateral etch rates are comparable, whereas dry etching processes like sputter etching, plasma etching, ion beam etching, and reactive ion etching are anisotropic. Among the dry etching techniques, plasma and reactive ion etching are the most popular in semiconductor processing.

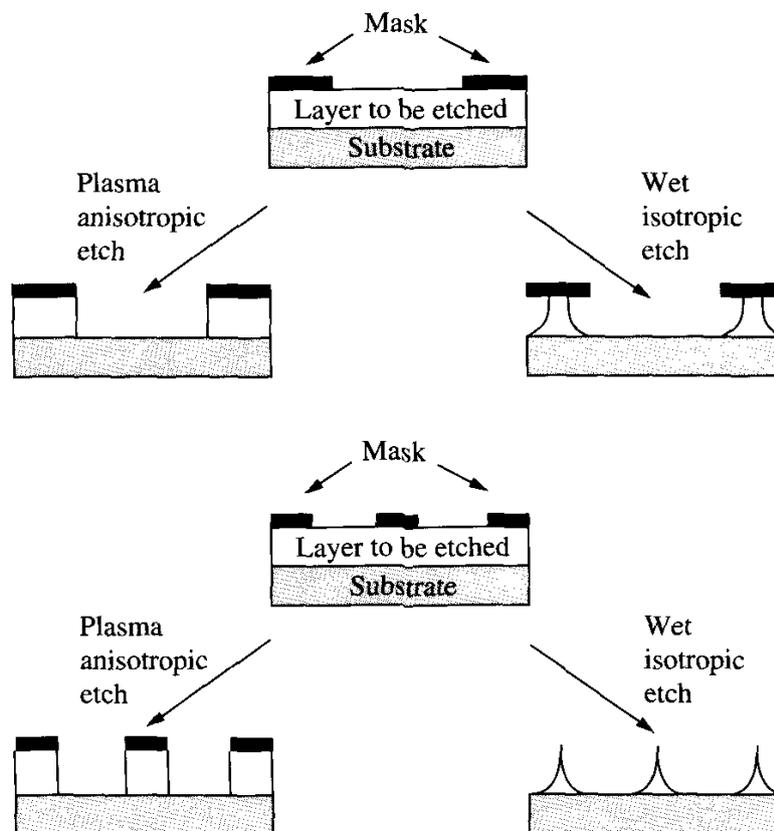


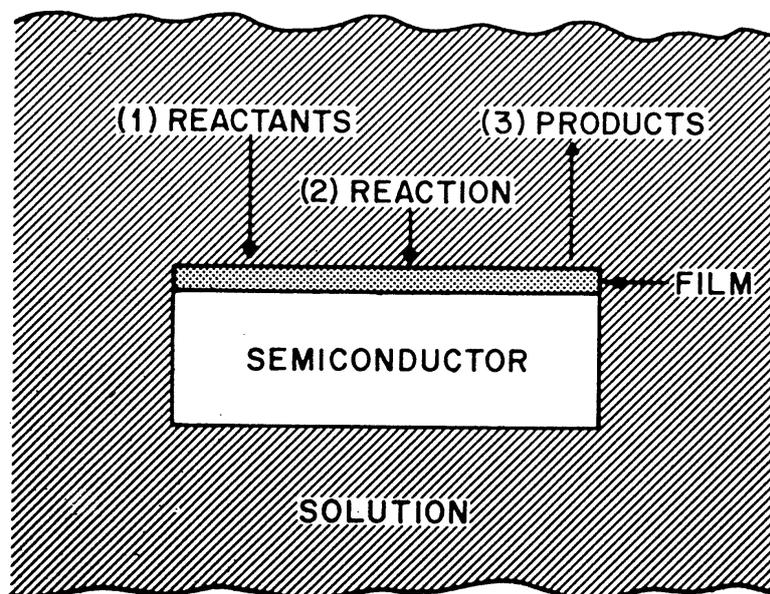
Figure 6.1: Difference between plasma (anisotropic) and wet (isotropic) etching.

6.1 Wet Chemical Etching

Wet chemical etching is employed in various processing steps. In wafer fabrication, chemical etching is used for lapping and polishing to give an optically flat, damage-free surface. Prior to thermal oxidation or epitaxial growth, wafers are chemically cleaned and scrubbed to remove contamination that results from handling and storing. For many discrete devices and integrated circuits of relatively large dimensions ($\geq 3 \mu$), chemical etching is used to delineate patterns and to open windows in insulating materials.

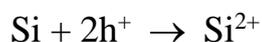
In IC processing, most chemical etchings proceed by dissolution of a material in a solvent or by converting the material into a soluble compound that subsequently dissolves in the etching medium. As illustrated in [Figure 6.2](#), wet chemical etching involves three essential steps:

- (1) Transportation of reactants to the reacting surface (e.g. by diffusion)
- (2) Chemical reactions at the surface
- (3) Transportation of the products from the surface (e.g. by diffusion)

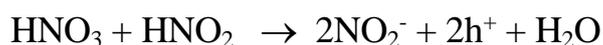


[Figure 6.2](#): Basic mechanisms in wet chemical etching.

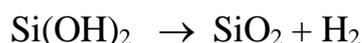
For semiconductor materials, wet chemical etching usually proceeds by oxidation, accompanied by dissolution of the oxide. For silicon, the most commonly used etchants are mixtures of nitric acid (HNO_3) and hydrofluoric acid (HF) in water or acetic acid (CH_3COOH). The reaction is initiated by promoting silicon from its initial oxidation state to a higher oxidation state:



The holes (h^+) are produced by the following autocatalytic process:



Si^{2+} combines with OH^- (formed by the dissociation of H_2O) to form $\text{Si}(\text{OH})_2$ which subsequently liberates H_2 to form SiO_2 :



SiO_2 then dissolves in HF:



The overall reaction can be written as:



Although water can be used as a diluent, acetic acid is preferred as the dissociation of nitric acid can be retarded in order to yield a higher concentration of the undissociated species.

At very high HF and low HNO_3 concentrations, the etching rate is controlled by HNO_3 , because there is an excess amount of HF to dissolve any SiO_2 formed. At low HF and high HNO_3 concentrations, the etch rate is controlled by the ability of HF to remove SiO_2 as it is being formed. The latter etching mechanism is isotropic, that is, not sensitive to crystallographic orientation.

Etching of insulating and metal films is usually performed with the same chemicals that dissolve these materials in bulk form and involves their conversion into soluble salts and complexes (*Table 6.1*). Generally speaking, film materials will etch more rapidly than their bulk counterparts. Moreover, the

etching rates are higher for films that possess poor microstructures or built-in stress, are non-stoichiometric, or have been irradiated.

Table 6.1: Etchants for Insulators and Conductors.

Material	Etchant Composition	Etch Rate
SiO ₂	28 ml HF 170 ml H ₂ O 113 g NH ₄ F	100 nm/min
	15 ml HF 10 ml HNO ₃ 300 ml H ₂ O	
	<i>Buffered HF</i>	
	<i>P – Etch</i>	12 nm/min
Si ₃ N ₄	<i>Buffered HF</i>	0.5 nm/min
	<i>H₃PO₄</i>	10 nm/min
Al	<i>1 ml HNO₃</i> <i>4 ml CH₃COOH</i> <i>4 ml H₃PO₄</i> <i>1 ml H₂O</i>	35 nm/min
Au	<i>4 g KI</i> <i>1 g I₂</i> <i>40 ml H₂O</i>	1 μm/min
Mo	<i>5 mg H₃PO₄</i> <i>2 ml HNO₃</i> <i>4 ml CH₃COOH</i> <i>150 ml H₂O</i>	0.5 μm/min
Pt	<i>1 ml HNO₃</i> <i>7 ml HCl</i> <i>8 ml H₂O</i>	50 nm/min
W	<i>34 g KH₂PO₄</i> <i>13.4 g KOH</i> <i>33 g K₃Fe(CN)₆</i> <i>H₂O to make 1 liter</i>	160 nm/min

6.2 Dry Etching

Many of the materials used in VLSI, such as SiO_2 , Si_3N_4 , deposited metals, and so on, are amorphous or polycrystalline, and if they are etched in a wet chemical solution, the etching mechanism is generally isotropic, that is, the lateral and vertical etch rates are the same (*Figure 6.3b*). However, in pattern transfer operations, a resist pattern is defined by a lithographic process (*Figure 6.3a*), and anisotropic etching is needed to yield steep vertical walls (*Figure 6.3c*). If h_f is assumed to be the thickness of the thin film and l the lateral distance etched underneath the resist mask, the degree of anisotropy, A_f , is defined to be:

$$A_f \equiv 1 - l / h_f = 1 - v_l / v_v \quad (\text{Equation 6.1})$$

where v_l and v_v are the lateral and vertical etch rates, respectively. For isotropic etching, $v_l = v_v$ and $A_f = 0$.

As illustrated in *Figure 6.3b*, the major disadvantage of wet chemical etching for pattern transfer is the undercutting of the layer underneath the mask, resulting in a loss of resolution in the etched pattern. In practice, for isotropic etching, the film thickness should be about one third or less of the resolution required. If patterns are required with resolution much smaller than the film thickness, anisotropic etching (i.e., $1 \geq A_f \geq 0$) must be used. *Figure 6.3c* depicts the limiting case when $A_f = 1$, corresponding to $l = 0$ or $v_l = 0$.

To achieve $A_f = 1$, dry etching methods have been developed. Dry etching is synonymous with plasma-assisted etching or reactive plasma etching, which denotes several techniques that employ plasma in the form of a low-pressure discharge.

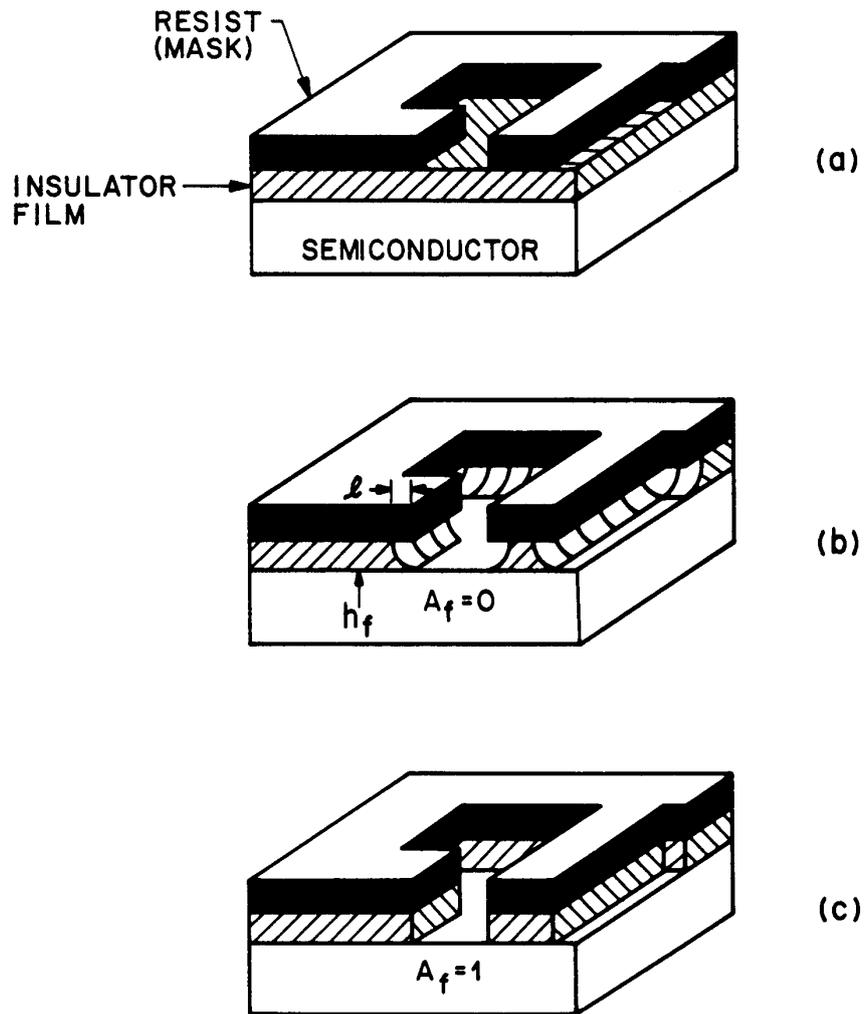


Figure 6.3: Comparison of wet chemical etching and dry etching for pattern transfer.

6.3 Plasma Excitation and Plasma - Surface Interaction

A plasma is a fully or partially ionized gas composed of ions, electrons, and neutrals. The plasma most useful to ULSI processing is a weakly ionized plasma called glow discharge containing a significant density of neutral particles (>90% in most etchers). Although plasma is neutral in a macroscopic sense, it behaves quite differently from a molecular gas, because it consists of charged particles that can be influenced by applied electric and magnetic fields.

A plasma is produced when an electric field is applied across two electrodes between which a gas is confined at low pressure, causing the gas to break down and become ionized (*Figure 6.4*). Simple DC (direct current) power can be used to generate plasma, but insulating materials require AC (alternate current) power to reduce charging. In plasma etching, an RF (radio frequency) field is usually used to generate the gas discharge. One reason for doing so is that the electrodes do not have to be made of a conducting material. The other reason is that electrons can pick up sufficient energy during field oscillation to cause more ionization by electron – neutral atom collisions. As a result, the plasma can be generated at pressures lower than 10^{-3} Torr.

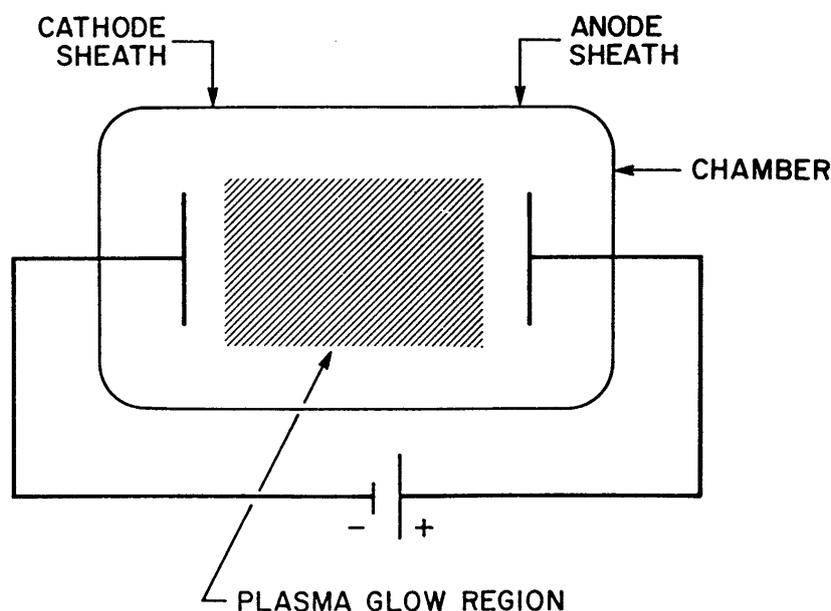
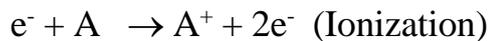
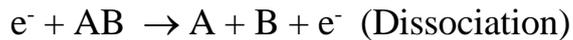
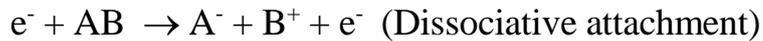


Figure 6.4: Schematic representation of a dc glow discharge showing the glow and sheath regions when the cathode and anode are closely spaced. As the spacing is increased, the plasma structure becomes more complex.

The free electrons released by photo-ionization or field emission from a negatively biased electrode create the plasma. The free electrons gain kinetic energy from the applied electric field, and in the course of their travel through the gas, they collide with gas molecules and lose energy. These inelastic collisions serve to further ionize or excite neutral species in the plasma via the following reaction examples:



Some of these collisions cause the gas molecules to be ionized and create more electrons to sustain the plasma. Therefore, when the applied voltage is larger than the breakdown potential, the plasma is formed throughout the reaction chamber. Some of these inelastic collisions can also raise neutrals and ions to excited electronic states that later decay by photoemission, thereby causing the characteristic plasma glow.

The interaction of plasmas with surfaces is often divided into two components: physical and chemical. A physical interaction refers to the surface bombardment of energetic ions accelerated across the plasma sheath. Here the loss of kinetic energy by the impinging ions causes ejection of particles from the sample surface. Conversely, chemical reactions are standard electronic bonding processes that result in the formation or dissociation of chemical species on the surface.

As exhibited in [Figure 6.5](#), the plasma-assisted etching process proceeds in several steps. It commences with the generation of the etchant species in the plasma, accompanied by diffusion of the reactant through the dark sheath to the specimen surface. After the reactant adsorbs on the surface, chemical reactions and/or physical sputtering occur to form volatile compounds and/or atoms that are subsequently desorbed from the sample surface, diffuse into the bulk gas, and pumped out by the vacuum system.

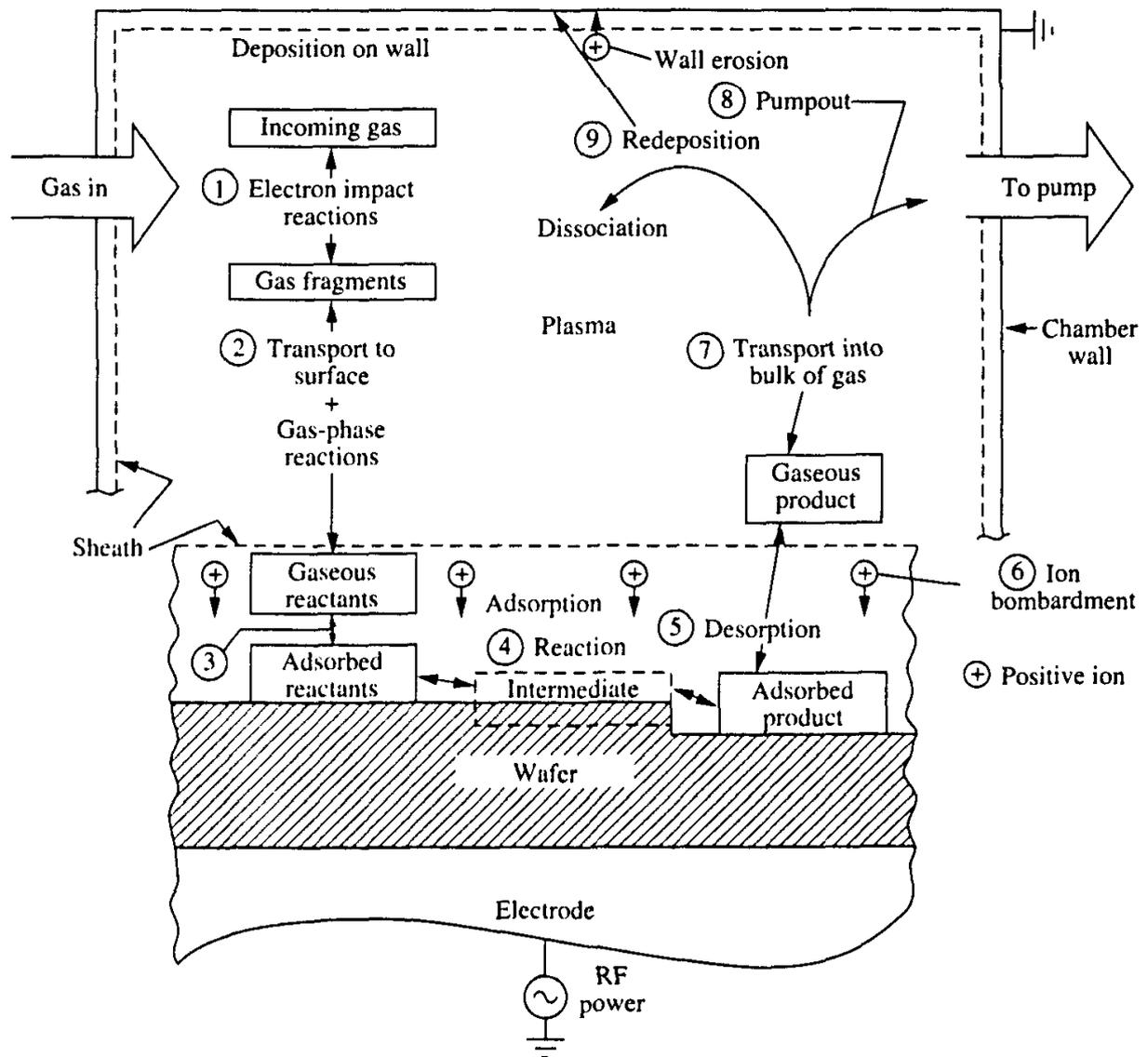


Figure 6.5: Schematic view of the microscopic processes that occur during plasma etching of a silicon wafer.

6.4 Simple Plasma Etching Systems

Figure 6.6 depicts two simple dry-etching systems. *Figure 6.6(a)* is the schematic of a sputtering - etching system utilizing relatively high energy (≥ 500 eV) noble gas ions such as argon. The wafer to be etched (called target) is placed on a powered electrode, and argon ions are accelerated by the applied electric field to bombard the target surface. Through the transfer of momentum, atoms near the surface are sputtered off the surface. The typical operating pressure for sputter etching is 0.01 to 0.1 Torr. The direction of the electric field is normal to the target surface and under the operating pressure, argon ions arrive predominantly normal to the surface. Consequently, there is essentially no sputtering of the sidewalls and a high degree of anisotropy can be attained. However, a major drawback for sputter etching is its poor selectivity, for the ion bombardment process etches everything on the surface, albeit the difference in sputtering rates for different materials.

Figure 6.6(b) depicts the schematic of a parallel - plate plasma etching system. The plasma is confined between the two closely spaced electrodes. Molecular gases containing one or more halogen atoms are fed through the gas ring. The typical operating pressure is relatively high, from 0.1 to 10 Torr.

An alternative plasma etching method is reactive ion etching (RIE), which employs apparatus similar to that for sputter etching shown in *Figure 6.6(a)*. The primary difference here is that the noble gas plasma is replaced by a molecular gas plasma similar to that in plasma etching. Under appropriate conditions, both RIE and plasma etching can give high selectivity and a high degree of anisotropy.

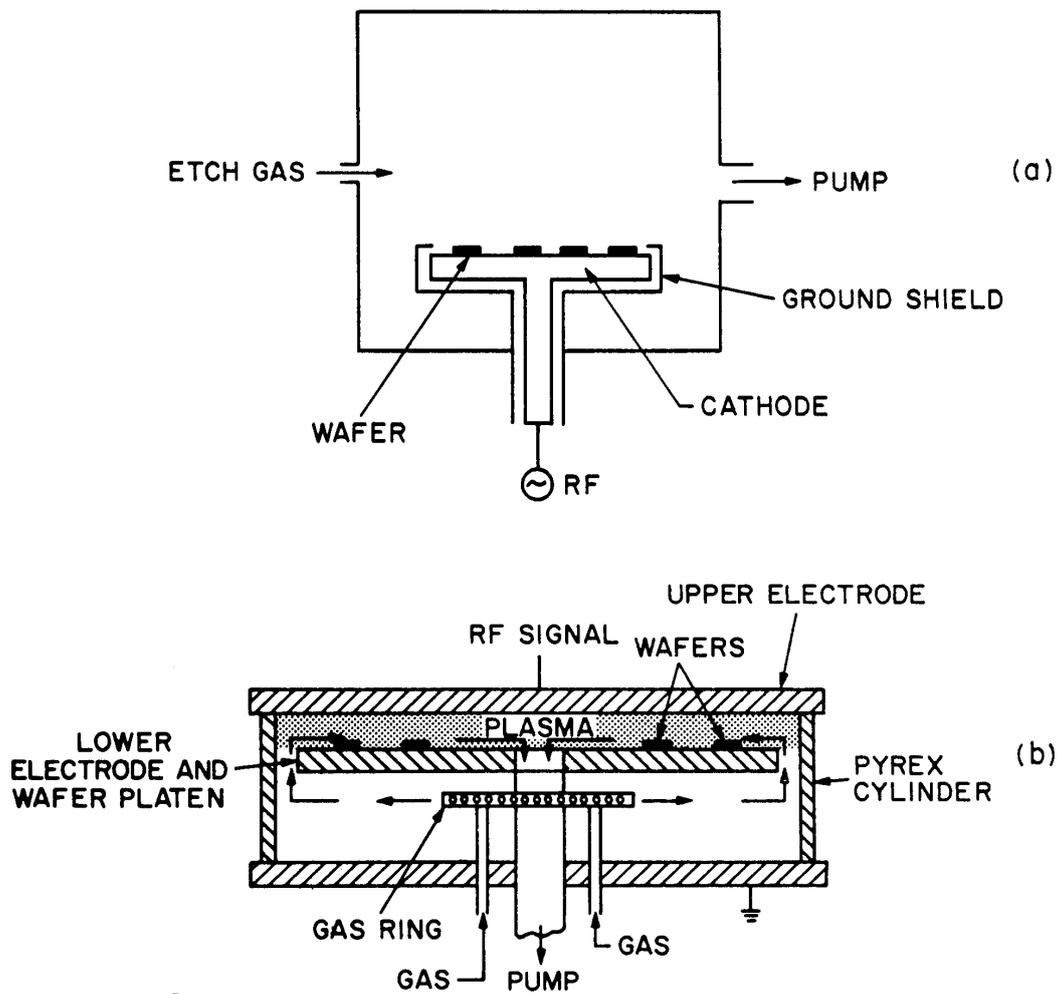


Figure 6.6: (a) A sputtering – etching system. (b) A parallel – plate, plasma – etching system.

6.5 Examples of Etching Reactions

In both plasma and reactive ion etching, ions from the plasma are attracted to the sample surface. However, the pure sputtering process is quite slow. The etching rate can be enhanced substantially by ion-assisted chemical reactions. *Figure 6.7(a)* depicts the etch rate as a function of flow rate of XeF_2 molecules with and without 1 keV Ne^+ bombardment. The lateral etch rate depends only on the ability of XeF_2 molecules to etch silicon in the absence of energetic ions impacting the surface, whereas the vertical etch rate is a synergistic effect due to both Ne^+ bombardment and XeF_2 molecules. The degree of anisotropy can generally be enhanced by increasing the energy of the ions.

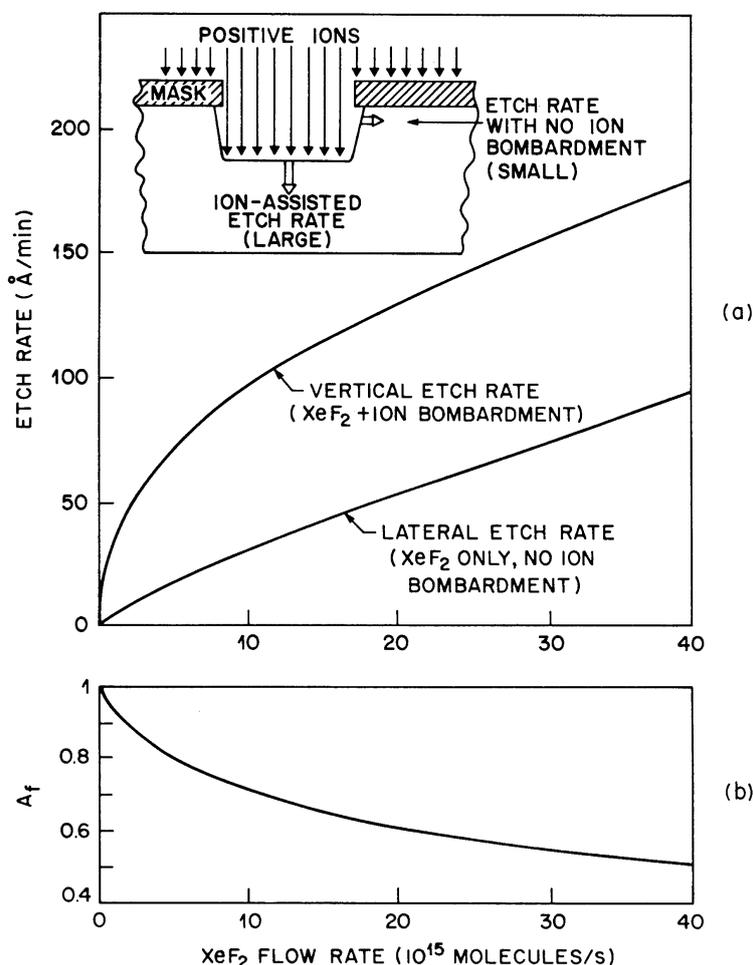


Figure 6.7: Silicon etching rate versus XeF_2 flow rate with and with 1-keV Ne^+ bombardment. Insert shows the ion-assisted reaction in the vertical direction.

When a gas is mixed with one or more additive gases, both the etch rate and selectivity can be altered. As illustrated in [Figure 6.8](#), the etching rate of SiO_2 is approximately constant for addition of up to 40% hydrogen, while the etch rate for silicon drops monotonically and is almost zero at 40% H_2 . Also shown is the selectivity, that is, the ratio of the etch rate silicon dioxide to that of silicon. Selectivity exceeding 45:1 can be achieved with $\text{CF}_4 - \text{H}_2$ reactive ion etching. This process is thus useful when etching a SiO_2 layer that covers a polysilicon gate.

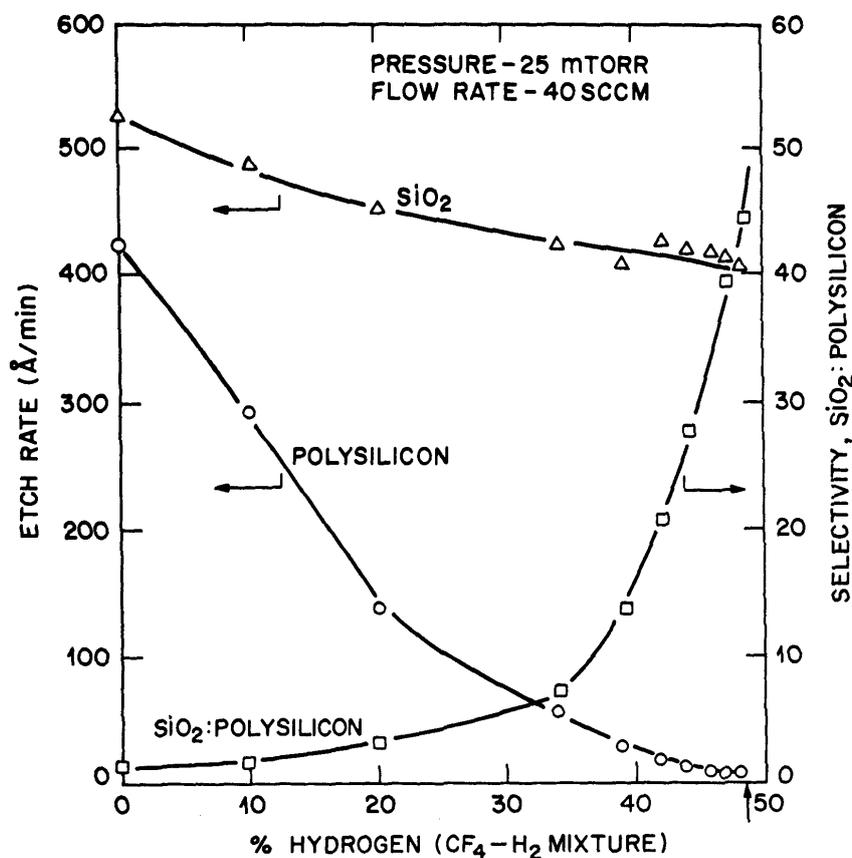


Figure 6.9: Etching rates of Si and SiO_2 and the corresponding selectivity as a function of percent H_2 in CF_4 .

The opposite effect can be observed by varying the gas composition of sulfur hexafluoride (SF_6) and chlorine, as exhibited in [Figure 6.9](#). The etching rate of silicon can be adjusted to be 10 to 80 times faster than that of silicon dioxide. Examples of some common etchants exhibiting selectivity effects are exhibited in [Table 6.2](#).

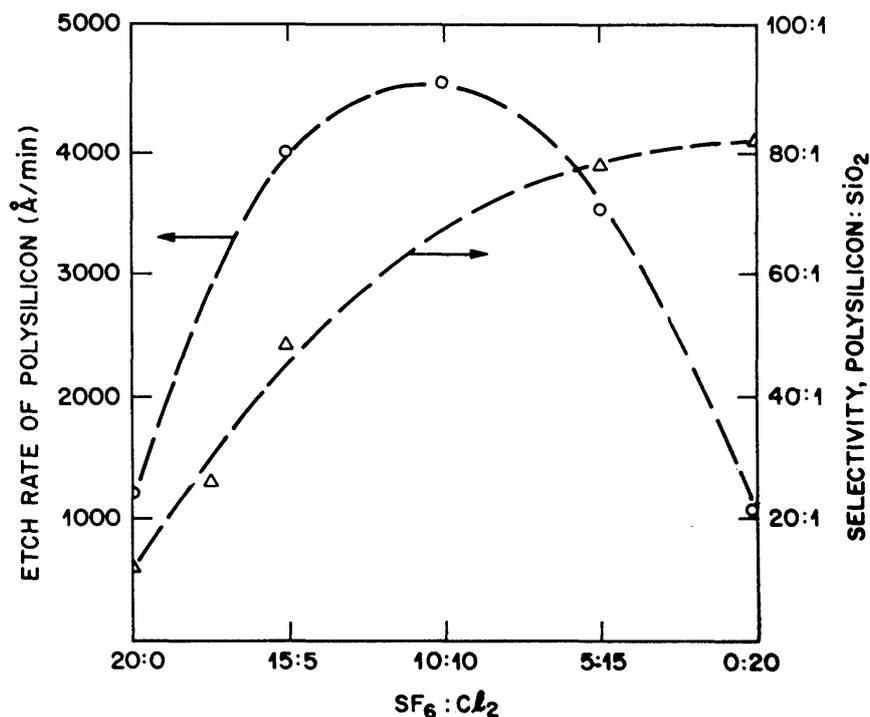


Figure 6.9: Dependence of etching rates of polysilicon and selectivity to SiO₂ as a function of the gas composition in SF₆ – Cl₂ (at 5.5 Pa).

Table 6.2: Etch Rates and Selectivities for Dry Etching.

Material (M)	Gas	Etch Rate (Å/min)	Selectivity		
			M/Resist	M/Si	M/SiO ₂
Si	SF ₆ + Cl ₂	1000-4500	5	-	80
SiO ₂	CF ₄ + H ₂	400-500	5	40	-
Al, Al-Si, Al-Cu	BCl ₃ + Cl ₂	500	5	5	25

Figure 6.10(a) illustrates the lift-off technique which has been discussed in the previous chapter. This technique has two distinct disadvantages:

- (a) Rounded feature profile
- (b) Temperature limitations ($\leq 200^{\circ}\text{C}$ to 300°C)

A more desirable technique is direct etching, which is shown in **Figure 6.10(b)**.

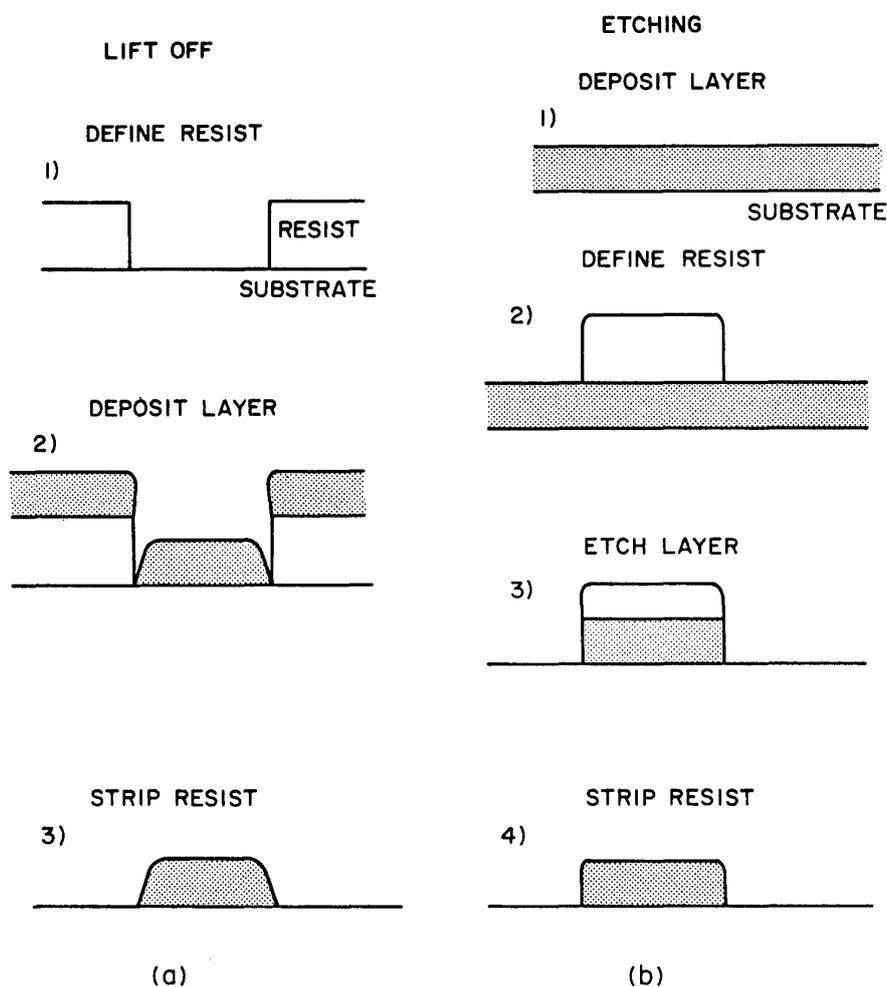


Figure 6.10: Schematic representation of two techniques for transferring resist features into a layer: **(a)** Resist / deposition strip sequence of lift off. **(b)** Deposit / resist / etch / strip sequence of etching.