

# Wet and Dry Etching

## Theory

### 1. Introduction

Etching techniques are commonly used in the fabrication processes of semiconductor devices to remove selected layers for the purposes of pattern transfer, wafer planarization, isolation and cleaning. There are two fundamental groups of etching: wet etching (liquid-based etchants) and dry etching (plasma-based etchants). Wet etching removes the materials by immersing the wafers in a chemical solution that reacts with selected films to form soluble by-products. It is easily implemented and cost-efficient, and it etches quickly. Sometimes, high selectivity can also be achieved. However, it is difficult to control, prone to high defect levels on wafers, inadequate for defining feature sizes that are smaller than  $1\mu\text{m}$ , and produces chemical waste. Due to these properties, wet etching is usually used for some noncritical processes such as wet cleaning (removal of  $\text{SiO}_2$  layer to obtain clean Si wafers). Dry etching, also called plasma etching, sputters or dissolves the materials using reactive ions in a gas phase. It utilizes plasma instead of liquid etchants to remove the materials, which is more precise, controllable and repeatable compared to wet etching, but a more expensive vacuum system is required. For instance, plasmas are easier to start and stop, and less sensitive to temperature; moreover, they are capable of defining feature sizes smaller than 100nm. In this module, you will perform both wet and dry etching experiments.

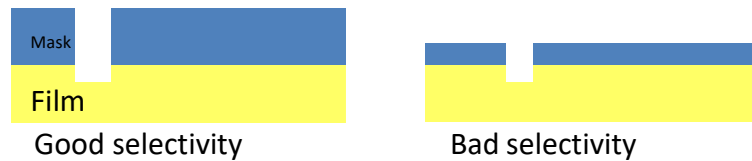
### 2. Theory

#### 2. 1. Etching metrics

**Etch rate** is defined as etched depth per unit time. Common desired etch rates are between 100 to 1000 angstroms per minute. If the etch rate is too high, the process will be difficult to control. However, in some cases, high etch rates are preferable for deep hole etching (i.e., anisotropic etch process which creates deep penetrating holes and trenches in wafers) or substrate removal.

**Uniformity** is the percentage variation of the etch rates across a wafer.

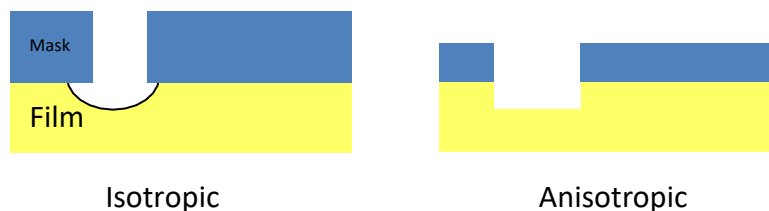
**Selectivity** is the ratio of the etch rates of one materials over the other. For example, the selectivity is ratio of the etch rate of the layer being etched to the etch rate of the mask or the layer under the layer being etched. Etching with high selectivity is supposed to remove the selected layer entirely without harming the substrate and mask. For example, KOH etches polysilicon over oxide, with selectivity 1000 to 1, which shows that the polysilicon can etch 1000 times faster than oxide [1].



## Anisotropy

- **Isotropic etching** has the same etch rate in all directions.
- **Anisotropic etching** has different etch rates in the lateral and vertical directions.

Anisotropic etching is preferable in semiconductor manufacturing processes. Most wet etching profiles are isotropic, except for etching crystalline materials, whereas etching profiles of dry etching are anisotropic.



Anisotropy is defined as

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

where  $R_L$  and  $R_V$  are the lateral and vertical etch rates, respectively. For perfectly anisotropic etching,  $A$  is 1. For perfectly isotropic etching,  $A$  is 0.

**Undercut** is the lateral distance per side under the mask, as shown in Figure 1. It can be characterized by the etch rate anisotropy  $A$ . Sometimes, the etchant will attack the photoresist pattern, which causes an etch bias.

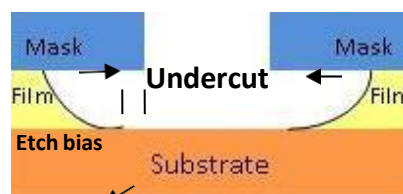


Figure 1. Undercut and etch bias

## 2.2. Wet etching

Wet etching is a purely chemical process that removes materials from a wafer using liquid-phase etchants.

### 2.2.1. Etchants

Most wet etchants consists of an oxidizing agent, an agent for dissolving the oxides, and a

solvent, such as water. The typical materials of the oxidizing agent are  $\text{H}_2\text{O}_2$ ,  $\text{Br}_2$ ,  $\text{AgNO}_3/\text{CrO}_3$ ,  $\text{HNO}_3$ , and  $\text{NaOCl}$ . The agents for dissolving the oxides can be an acid or base which can dissolve the oxidized layer, for example,  $\text{NH}_4\text{OH}$ ,  $\text{NaOH}$ ,  $\text{H}_2\text{SO}_4$ ,  $\text{HCl}$ ,  $\text{HF}$ , and  $\text{H}_3\text{PO}_4$ . The solvent is usually water or  $\text{CH}_3\text{COOH}$  to transport reactants and products.

### 2.2.2. Mechanisms and rate-limiting step

A wet etching process involves multiple chemical and physical processes, which are described in Figure 2. First, the etchant species is transported to the surface of the wafer. This process typically includes diffusion of the etchant towards the surface and adsorption of the etchant at active sites on the surface. Second, a chemical reaction between the etchant and the exposed surface happens; this then produces soluble by-products. Finally, the products of the reaction will desorb and move away from the surface by diffusion. The slowest step of these processes is called rate-limiting step, which can determine the etch rate.

If the thickness of the diffusion boundary layer is very small, the etching process will be determined by the chemical reaction step and become reaction-rate-limited. Diffusion-limited etching often occurs in viscous solutions which consist of high concentrations of the agent for dissolving the oxides and low concentrations of the oxidizing agent. The etch rate at the mask edge will be enhanced as the concentration of the etchant at the edge is higher, especially for diffusion-limited etching. Figure 3 shows the step height profilometer traces of GaAs surface etched with the  $\text{H}_2\text{SO}_4\text{-H}_2\text{O}_2\text{-H}_2\text{O}$  based etchant on GaAs surface. For the 1:1:16 etchant, the step height profile is flat since the process is reaction-rate-limited. However, for the etchant concentration of 10:1:1, the etch process becomes diffusion-limited; therefore, the etched area is deeper at the edge.

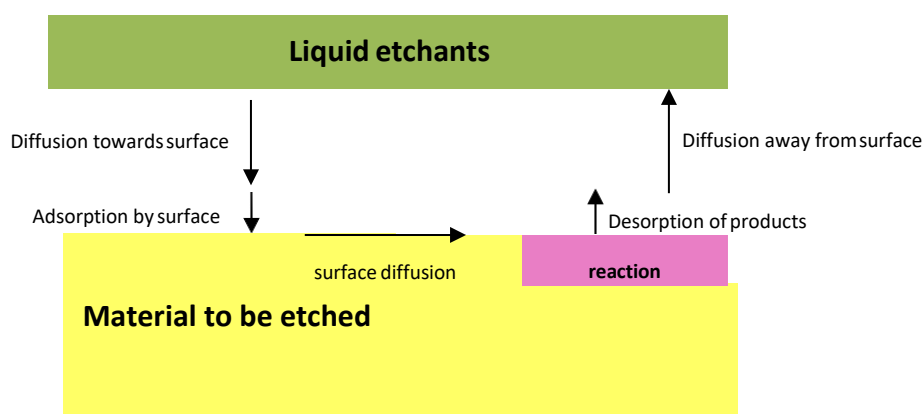


Figure 2. Wet etching mechanisms

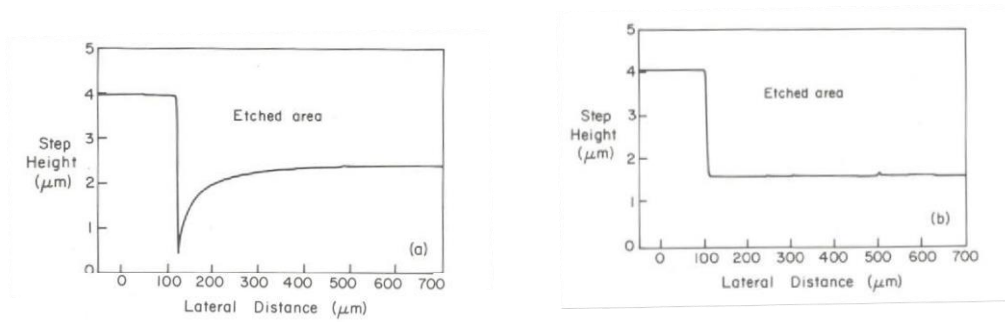


Figure 3. Step height profilometer traces of two compositions of  $\text{H}_2\text{SO}_4\text{-H}_2\text{O}_2\text{-H}_2\text{O}$  etchants on GaAs, showing (a) enhanced etching at the mask edge for 10:1:1, and (b) a flat-bottomed shape for 1:1:16. Note that a flat profile is obtained only when the distance between the mask edge and material to be etched is smaller than  $400\mu\text{m}$  [2].

### 2.2.3. Temperature dependence and agitation dependence

The main factors controlling the etch rate are temperature and agitation. In a reaction-limited etching process, the etch rate shows a stronger dependence on the temperature than in a diffusion-limited etching processes. The relationship between etch rate  $R$  and temperature  $T$  can be described by the Arrhenius equation:

$$R = R_0 e^{-E_A/kT},$$

where  $R_0$  is the rate constant that depends on the density and diffusivity of reactants,  $E_A$  is the activation energy, and  $k$  is the Boltzmann constant. To obtain parameters of the Arrhenius equation, a graph is plotted for  $\ln R$  vs  $1/T$ . The slope of this graph is  $(-E_A/k)$  and the pre-exponential factor  $R_0$  is obtained from the intercept of this graph.

High activation energy (greater than 20 KJ/mol) indicates that the etching is reaction-limited, whereas lower activation energy means diffusion-limited etching occurs. Usually reaction rate-limited etching is preferred to diffusion limited etching because it is easier to control comparatively as external agitation is not required and hence is repeatable. For a diffusion-limited etching condition, adequate agitations will help generate a large, uniform and well-controlled etch rate, since the agitation-induced turbulence will decrease the thickness of diffusion boundary layer. However, for a reaction-rate-limited process, agitation makes no change in etch rates.

If the products of an etching process are gases, some bubbles will be formed in the solution, which may reduce the transport rate of etchants. In this case, adequate agitations can assist the movement of etchants into the surface.

Figure 4 shows effects of both temperature and agitation on the rate of a diffusion-limited etching processes. Stirring increases the pre-exponential factor  $R_0$ . However, it does not affect the activation energy  $E_A$ . Therefore, the Arrhenius plots for reactions with and without stirring have the same slopes but different intercepts.

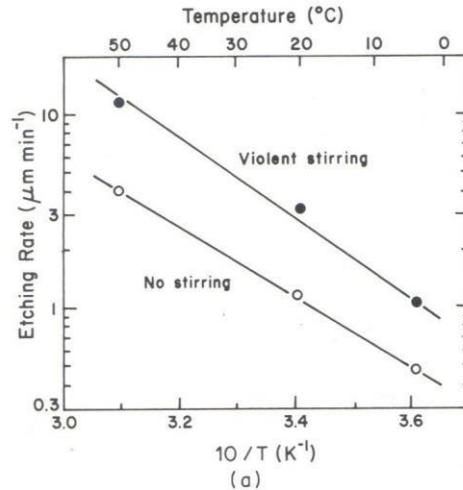


Figure 4. Temperature and agitation dependence of diffusion-limited etching processes, showing the Arrhenius plot in (100) GaAs using H<sub>2</sub>SO<sub>4</sub>-H<sub>2</sub>O<sub>2</sub>-H<sub>2</sub>O etchant (8:1:1) [3].

#### 2.2.4. Etching profile

The shapes of etching sidewalls usually depend upon the orientation of the etched materials and etching conditions. Figure 5 shows three types of etching sidewall shapes: rectangular-shaped, positive sloping and negative sloping. For example, gradually positive sloping edges are more desirable, which allows continuous interconnection metal been deposited over the positive slope mesas. Rectangular-shaped sidewalls can lead to reduced conformal thicknesses and cause discontinuous films. On films with negative sloping sidewalls, one is also unable to deposit continuous interconnect metallization. Figure 6 shows an unsuitable etched profile produced by most reaction-rate-limited processes. Diffusion-limited etching tends to produce sloping edges; however, it will result in a severe trenching problem and is also considered undesirable.



Figure 5. Etching sidewall shapes: (a) rectangular-shaped, (b) positive sloping, and (c) negative sloping [4].

Wet etching of polycrystalline materials like silicon is usually anisotropic because etchants like Potassium hydroxide (KOH) display an etch rate selectivity 400 times higher in the <100> crystal direction than in the <111> direction. An anisotropic wet etch on a silicon wafer creates a cavity with a trapezoidal cross-section. The bottom of the cavity is a {100} plane, and the sides are {111} planes, see Fig. 6d.

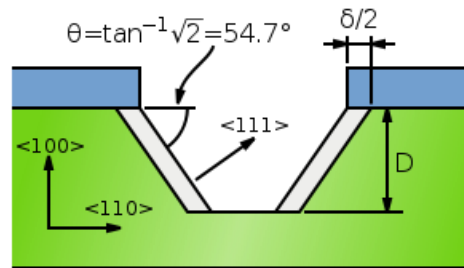


Figure 6. Anisotropic wet etch on Si wafer [5]. The blue material is an etch mask, and the green material is silicon.

In our lab, we perform wet etching using BOE and KOH as etchants. BOE is used to etch the  $\text{SiO}_2$  layer, while KOH is used to etch the underlying Si layer. We also determine if KOH etching of Si is a reaction- or diffusion-limited process.

### 2.3. Dry etching

Dry etching is one of the most widely used processes in semiconductor manufacturing since it is easier to control, is capable of defining feature sizes smaller than 100 nm, and produces highly anisotropic etching. It may remove the materials by chemical reactions (using chemical reactive gases or plasma), by purely physical methods (e.g., sputtering and ion beam-induced etching), or with a combination of both chemical reaction and physical bombardment (e.g., reactive ion etching).

#### 2.3.1. Plasma

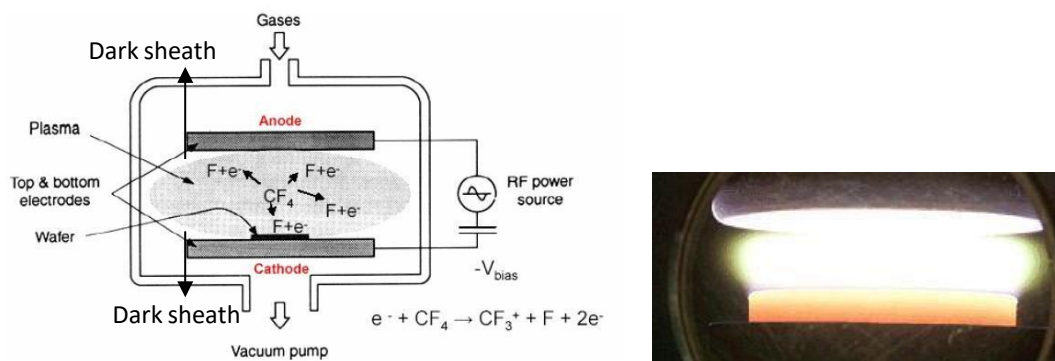
Plasma is a partially ionized gas composed of equal numbers of positive and negative charges, as well as some neutral molecules. Plasma can be generated by applying a strong radio frequency (RF) electromagnetic field to a gas, which breaks down gas molecules and generates ions, free radicals, electrons, photons and reaction by-products such as ozone. Since these reactive species have high energy, they create highly active and low-temperature plasma which can etch materials precisely and efficiently. Some practical applications of plasma include clearing surface films and sputtering materials into a surface.

#### 2.3.2. Dry etching mechanisms

The mechanism of dry etching is very similar to the wet etching mechanism. First, a feed gas is introduced into the chamber, where it is broken down into chemically reactive species to form plasma. Reactive species diffuse to the surface to be etched and are then adsorbed on this surface. Once the reactive species reach the surface, they move around on the surface (this process is called surface diffusion) until they react with the exposed film. Afterwards, products of the reaction will desorb from the surface and diffuse away through the gas stream. In some cases, the sample chuck temperature is intentionally elevated to increase volatility of the products.

### 2.3.3. Reactive ion etching (RIE)

RIE combines physical processes with chemical reactions. It uses a chemically reactive plasma generated under a low pressure (10-100 mTorr) to consume the materials deposited on wafers, along with non-reactive ionic bombardment which can make certain areas on the wafer accessible for chemical reactions. In the RIE system, the chuck holding wafer is grounded and another electrode is connected to the RF power source (see Figure 7). Generally, the frequency is 13.56 MHz. Since electrons are more mobile compared to positive ions due to their lighter weight, they travel longer distances and collide more frequently with the electrodes and chamber walls and are consequently removed from the plasma. This process leaves the plasma positively charged. Nevertheless, plasma tends to remain neutral charged; thus, a DC electric field is formed [6]. The region of surfaces in the chamber and electrodes, shown in Figure 7, is called “dark sheath”. Besides the chemical reaction between the plasma and the target material, the positive ions can be accelerated across the dark sheath by electrical field and strike the target material. This process is the physical bombardment which can also assist the etching process. In addition, in contrast to the wet chemical etching, RIE has a higher probability to move the etchants in the direction of the electric field and produces more anisotropic etch profiles.



In our lab, reaction ion dry etching is used to etch Si and SiO<sub>2</sub>. Argon is the purge gas and SF<sub>6</sub> gas is the etchant gas.

### 2.3.4. Inductively Coupled Plasma etching (ICP)

The ICP employs radio frequency generated by the electromagnetic induction coil to create plasma of ionized atoms and radicals capable of etching various semiconductor materials. As to the geometry and operation of ICP, the induction coil of the ICP is wrapped two or three times around the torch (a concentric quartz structure shown in Fig. 8) and has water flowing through it for cooling purposes. In order for the RF power to travel along the surface of the coil with minimum resistance, all ICPs have a capacitor bank, which is continuously tuned to match the plasma's inductance. The RF power supply maintains the plasma and the Tesla coil is used to ignite the plasma through the generation of electrons and ions, which couple with

the magnetic field. Very high plasma densities can be achieved by ICP and the etch profiles tend to be more isotropic than RIE.

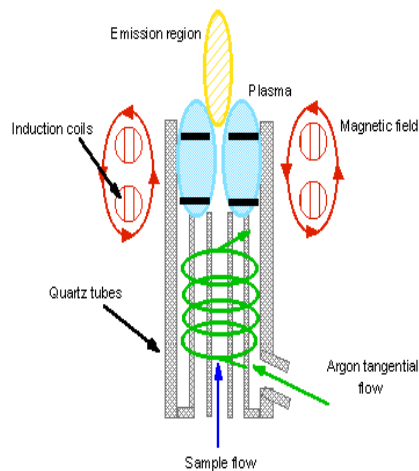


Fig 8 ICP Torch and ICP Schematic [8]

Currently, the combination of typical RIE (parallel plate) and inductively coupled plasma RIE is possible. In this system, the ICP is employed as a high density source of ions which increases the etch rate, whereas a separate RF bias is applied to the substrate to create directional electric fields near the substrate to achieve more anisotropic profiles. However, it can also be run in RIE mode for certain low etch rate applications and control over selectivity and damages.

### 2.3.5. Ion Milling

Ion Milling [9] is a physical etching technique where ions of inert gas (typically Argon) are accelerated from wide beam ion source into the surface of the wafer in vacuum in order to remove material to some desired depth. The continuous bombardment of the substrate by ions results in conversion of kinetic to heat energy and subsequent heating of the substrate. Substrate cooling is often required to prevent damage. Some of the kinetic energy from the incident ions results in substrate atom(s) or secondary ions being driven away from the surface. Heating the substrate, or letting it heat up in vacuum due to the process itself, can in fact accelerate the etch rate as substrate heating adds energy to the surface particles allowing them to be ejected with less incident kinetic energy. This may also be undesirable since it is a runaway condition.

### References

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