PLASMA CHEMISTRY

Many chemical reactions of neutral gases with semiconductor materials can be accelerated in the presence of a plasma (1). Examples include etching of patterns into single- or polycrystalline Si using F_2- or Cl_2-based chemistries, removal of photoresist films in O_2 plasmas, etching of Al metallization in Cl_2-based plasmas, and patterning of compound semiconductors in various halogen (Cl_2, I_2, or Br_2) plasmas. The typical process takes advantage of the ability to tailor the vertical and horizontal etch rates of a film or substrate selectively masked by photoresist or dielectric and thus achieve high-fidelity pattern transfer. Alternatively, in some applications one simply wants to strip a film selectively from an underlying layer of a different material, and in this case an isotropic etch process is employed. There are many variants of plasma etching apparatus (2–4), ranging from simple barrel reactors in which etching occurs only through reactive neutral species (leading to isotropic etching) to systems involving an additional, significant flux of energetic ions arriving at the sample surface simultaneously with the reactive neutrals. The effect of these ions is to enhance greatly the adsorption of the reactive neutrals by providing "active" sites, the subsequent reaction of the adsorbed species with the sample (for example, by breaking bonds in the materials), or desorption of the etch product by essentially sputtering it from the surface. Of course, the latter step exposes a fresh surface for the process to be repeated all over again, producing a synergy between the chemical and physical component of the etching process and leading to a material etch rate larger than the sum of the two-individual components. A schematic of a sample in an ion-assisted etch system is shown in Fig. 1.

MODEL SYSTEM: F_2-BASED ETCHING OF SiO_2

The most common variant of the anisotropic (i.e., ion assisted) etching techniques is called reactive ion etching (RIE), and some typical characteristics of plasmas in this mode are shown in Table 1 (3). In Si device technology there are many dry etching steps involved, with requirements ranging from formation of deep (>6 μm), narrow (<0.5 μm) trenches for storage capacitors in the Si wafer to polysilicon/polycide gate definitions, where very high selectivity over a thin underlying oxide is required.

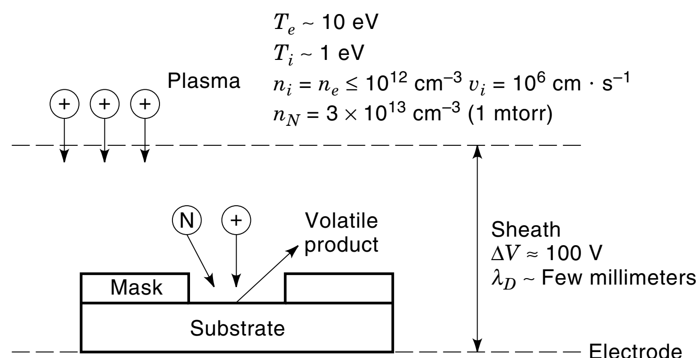


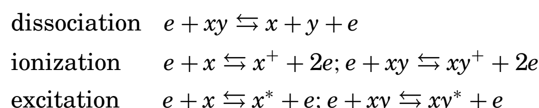
Figure 1. Schematic of sample geometry in an ion-enhanced etch reactor showing impingement of ions and neutral reactive atoms.

J. Webster (ed.), *Wiley Encyclopedia of Electrical and Electronics Engineering*. Copyright © 1999 John Wiley & Sons, Inc.

Table 1. Typical Characteristics of Low Pressure Plasmas Used for Reactive Ion Etching

Quantity	Typical Values
rf Power density	0.5–1.0 W/cm^2
rf Frequency	10 kHz–27 MHz (commonly 13.56 Hz)
Pressure	0.01–0.2 torr
Gas flow	10–200 sccm
Wafer temperature	−120°C up to 300°C
Gas temperature	300–600 K
Electron temperature	3–30 eV (bulk of plasma)
Ion energies	∼.05 eV (bulk of plasma)
	10–500 eV (after traversing cathode sheath)
Gas number density	3.5×10^{14}–7×10^{15} cm^{-3}
Ion density	10^{9}–10^{10} cm^{-3}
Electron density	Similar to ion density
Ion flux	10^{14}–10^{15} cm^{-2} s^{-2}
Radical flux	10^{16} cm^{-2} s^{-1}
Neutral flux	3.6×10^{18}–7.2×10^{19} cm^{-2} s^{-1}

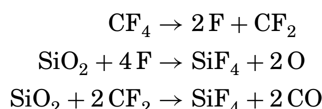
Since a plasma is a partially ionized gas, there are a number of different processes occurring in the gas phase. For example, for a molecule *xy*, the following may occur due to electron collisions:



$$\text{dissociation} \quad e + xy \leftrightarrows x + y + e$$
$$\text{ionization} \quad e + x \leftrightarrows x^+ + 2e;\ e + xy \leftrightarrows xy^+ + 2e$$
$$\text{excitation} \quad e + x \leftrightarrows x^* + e;\ e + xy \leftrightarrows xy^* + e$$

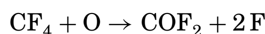
where x^+, xy^* are ions and x^+, xy^* are radicals or species whose energy is much larger than the ground state, and thus are very reactive because of their incomplete bonding state.

The major application of dry etching of SiO_2 is to pattern contact holes to underlying Si and to create via connection holes between various levels of metal in a multilevel metallization. The basic plasma chemistry for SiO_2 is based on fluorocarbon gases. The etch products are therefore SiF_4 and CO or CO_2 (5–9). The etch reactions may therefore be written as



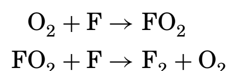
$$CF_4 \rightarrow 2\,F + CF_2$$
$$SiO_2 + 4\,F \rightarrow SiF_4 + 2\,O$$
$$SiO_2 + 2\,CF_2 \rightarrow SiF_4 + 2\,CO$$

Atomic fluorine reacts rapidly with Si, but its reaction rate with SiO_2 is orders of magnitude lower. The amount of free fluorine in the discharge may be increased by adding oxygen (4). That is,



$$CF_4 + O \rightarrow COF_2 + 2\,F$$

If the amount of oxygen addition is too great, the etch rates may decrease because of gas phase recombination through the reactions (4)



$$O_2 + F \rightarrow FO_2$$
$$FO_2 + F \rightarrow F_2 + O_2$$

By contrast, the concentration of free fluorine radicals may be decreased by addition of H_2, rather than O_2, to the fluorine-based plasma, the recombination of hydrogen and fluorine to form HF. As small concentrations of O_2 are added to CF_x, the etch rates of both SiO_2 and Si are increased, but not at the same rate. Thus it is possible to achieve high etch rates (or selectivity) for Si relative to SiO_2. By contrast, as H_2 is added to CF_4, the etch rate of Si falls much more quickly than that of SiO_2, producing high selectivity for SiO_2 in the absence of ion bombardment, but CF_x species can etch SiO_2 through the reactions noted previously.

The two main factors determining the selectivity for etching SiO_2 over Si are the deposition of the carbon-based polymer residue and the role of oxygen in the etching process. If a thick, nonvolatile polymer deposits on a surface, it will inhibit chemisorption of reactive species and quench the etching process. However, a lesser amount of polymer forms on SiO_2 than on Si because the carbon in the polymer can react to form volatile CO and CO_2. Therefore, SiO_2 can continue to etch even as the etching of Si is completely prevented by the polymer formation. Selectivities for SiO_2 over Si greater than 20 are readily achievable by this method. The ion-induced reactions in a CF_4/H_2 chemistry typically require a minimum ion bombardment energy of 100–200 eV (10–14).

Much of the data on etching the Si/SiO_2 system is explainable by considering the F/C ratio in the plasma chemistry. The Si etch rate is faster at higher F/C ratios, which can be created by altering the gas mixture (such as by O_2 addition). At low F/C ratios, obtained with CHF_3, C_3F_8, C_2F_6, or CF_4/H_2, there is high selectivity for SiO_2 over Si. Note that frequent chamber cleaning is required with polymer-forming chemistries to reduce particle counts. Most selective etching of SiO_2 is now based on CHF_3 with Ar or He as a diluent and a more fluorine-rich compound (e.g., C_2F_6 or CF_4) as a moderator. A typical process might involve varying the F/C ratio as endpoint is neared to enhance selectivity.

Generally, in the set of plasma etching conditions optimized for selective SiO_2 removal, it is difficult to achieve selective etching of SiN_x relative to either SiO_2 or Si. This is due to the fact that the nitride has bond strength and electronegativity between the other two materials. It is possible to etch SiN_x selectively over oxide by reducing the ion bombardment energy or by employing very H_2-rich chemistries.

There are three basic mechanisms for achieving selectivity of one material over another (3):

1. Selective formation of an etch-inhibiting layer on one of the materials (i.e., the situation where deposition is occurring on one material, while the other is etched under the same conditions)
2. Nonreactivity of one of the materials in the particular plasma chemistry employed, such as removal of resist films in an O_2 plasma that does not etch the underlying Si or SiO_2
3. Nonvolatility of a reaction product, such as formation of the nonvolatile AlF_3 on the surface of AlGaAs upon removal of an overlying GaAs layer in BCl_3/SF_6 or equivalent chemistry (15,16). Selectivity is nearly always decreased by increasing ion bombardment energy because this accelerates the adsorption, reaction, and desorption steps that initially produce the selective etching (17–20).

ETCHING OF Si

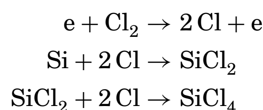
Table 2 shows the range of plasma chemistries typically employed for plasma etching of Si (21). There are two basic areas

Table 2. Etch Chemistries for Si (After Ref. 21)

Category	Comments
Primary Gases	
CF_4	Isotropic with added O_2, low etch rate without O_2. Relative low selectivity over SiO_2 (with O_2), compared to low-pressure, high-density Cl_2/O_2 plasmas.
SF_6	Isotropic except at very low pressure and/or substrate temperature. Relatively low selectivity over SiO_2, compared to low-pressure, high-density Cl_2/O_2 plasmas.
CCl_4, CF_2Cl_2	Anisotropic under most conditions. O_2 or Cl_2 addition prevents polymer formation.
$SiCl_4$	Addition of Cl_2 increases etch rate to acceptable levels.
Cl_2	Anisotropic under all conditions, except for n^+ Si.
Br_2, HBr	Slightly higher rates and selectivity over SiO_2, compared to Cl_2.
Additives	
Cl_2	Added to CCl_4, CF_2Cl_2 to increase etch rate, minimize polymer formation.
O_2	Increases selectivity over SiO_2 when added to Cl_2.
HBr	Sometimes added to Cl_2 to increase etch rate and selectivity.
BCl_3	Sometimes needed to break through native oxide and to scavenge H_2O.

of application. The first is etching of high aspect ratio (depth-to-width ratio) trenches or grooves for vertical capacitors in dynamic random access memory integrated circuits, or for circuit isolation. The second major application is patterning of polycrystalline Si for gates and high-temperature interconnects in metal oxide semiconductor (MOS) technology. For some applications metal silicides or refractory metals have replaced poly-Si, and these materials are covered later.

The trenches for isolation or capacitor formation are deep (3 to 6 μm) and need excellent verticality and clean, smooth sidewalls. The need for subsequent filling and planarization steps also requires a V-shaped bottom of the trench. Oxide masks are generally used because resist degrades at the high biases needed to produce high etch rates and vertical sidewalls. F_2-based plasma chemistries are often not the best suited for trench etching because of the difficulty in obtaining anisotropy without extensive polymer-sidewall protection, which leads to difficulties in maintaining constant etch rates as the aspect ratio of the trench increases with etch time (this is usually called reactive ion etch lag, in which narrow features etch slower, or aspect-ratio dependent etching; see Ref. 22). Chlorine-based plasmas etch Si by an ion-assisted mechanism, so that vertical sidewalls without undercut are achievable (23–26). The $SiCl_4$ etch product is less volatile than SiF_x and hence requires ion assistance to desorb. The basic reaction is therefore (4)



$$\mathrm{e} + \mathrm{Cl_2} \rightarrow 2\,\mathrm{Cl} + \mathrm{e}$$
$$\mathrm{Si} + 2\,\mathrm{Cl} \rightarrow \mathrm{SiCl_2}$$
$$\mathrm{SiCl_2} + 2\,\mathrm{Cl} \rightarrow \mathrm{SiCl_4}$$

Some have suggested that silicon subchlorides act to coat the trench sidewall and provide additional protection against undercut (4).

Undoped Si etches very slowly in Cl or Cl_2 in the absence of ion bombardment. However, heavily doped n-type Si etches spontaneously at high rates without ion bombardment in atomic Cl. This effect due to doping may be as high as a factor of 25 larger than undoped Si and is independent of the dopant species (27,28). This suggests that atomic Cl chemisorbed on Si does not break the underlying Si—Si bonds initially, but on an n-type surface will become negatively charged and can ionically bond with the Si. Undercut on n-type sidewalls can be eliminated through polymerization schemes, such as adding BCl_3, $SiCl_4$, CCl_4, or a fluorinated precursor to the Cl_2 plasma. A typical example of the latter is C_2F_6/Cl_2. Often the etch is initiated with BCl_3/Ar to remove the native oxide (29). The addition of O_2 to Cl_2 enhances selectivity over SiO_2, and bromine-based plasma chemistries (HBr or Br_2, mixed with Cl_2) may provide higher etch rate and selectivity over SiO_2 than for pure Cl_2 in high-density plasmas.

SF_6 may be used to etch Si anisotropically by adding an inert gas such as Ar to increase the ion-to-F flux impingement ratio, by adding a sidewall passivant to inhibit attach by F atoms, or by lowering the substrate temperature so that the SiF_4 etch product is longer volatile except where ions are desorbing it (30).

The most stable, fully halogenated etch products for Si are SiF_4 (boiling point −86°C), $SiCl_4$ (boiling point 57.6°C), and $SiBr_4$ (boiling point 154°C). Due to the ion-assisted desorption, subhalogen etch products may also play a significant role. The absolute reaction rate of F atoms with single crystal Si follows (9):

$$\mathrm{Rate}\ (\text{Å}\cdot\mathrm{min}^{-1}) = 2.9\times10^{-12}T^{1/2}N_{\mathrm{F}}\exp\left(\frac{-E_{\mathrm{F}}}{RT}\right)$$

where T is the absolute substrate temperature, N_F the F-atom number density, E_F the measured activation energy of 2.49 $\mathrm{kcal\cdot mol^{-1}}$, and R the gas constant. This equation represents the reaction of an F-saturated Si surface. At a pressure of 10 mtorr and 25°C, the etch rate would be 230 $\text{Å}\cdot\mathrm{min}^{-1}$, which would produce significant undercut. Cooling the substrate to −100°C would reduce this isotropic etch rate to 10 $\text{Å}\cdot\mathrm{min}^{-1}$. While substrate cooling is impractical for most manufacturing processes, it is usually necessary to employ He backside cooling of wafers during high-density plasma etching to avoid undercutting.

As mentioned previously, the reaction rate of Cl atoms is quite slow (~20 $\text{Å}\cdot\mathrm{min}^{-1}$ at 10 mtorr at 25°C) with undoped or p-type Si, but is higher for n^+ Si. For $n = 5\times10^{18}\ \mathrm{cm^{-3}}$ Si covered with Cl at steady state (31),

$$\mathrm{Rate}\ (\text{Å}\cdot\mathrm{min}^{-1}) = 7\times10^{8}P_{\mathrm{Cl}}\exp\left(\frac{-E_{\mathrm{Cl}}}{RT}\right)$$

where E_{Cl} has been measured as 6.64 $\mathrm{kcal\cdot mol^{-1}}$ (31). At 10 mtorr and 25°C, the etch rate is 100 $\text{Å}\cdot\mathrm{min}^{-1}$. Similarly, for Br_2 etching (32),

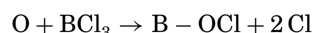
$$\mathrm{Rate}\ (\text{Å}\cdot\mathrm{min}^{-1}) = 10^{12}P_{\mathrm{Br}}\exp\left(\frac{-E_{\mathrm{Br}}}{RT}\right)$$

where E_{Br} is 14.8 kcal · mol^{-1}. Due to this large activation energy, undercutting is much less severe in Br_2-based plasma chemistries. HBr (and sometimes also O_2) may be added to Cl_2 during the entire etch process for selective etching of Si over SiO_2, or in many cases this addition is incorporated just prior to reaching the SiO_2 layer.

ETCHING OF Al AND Al ALLOYS

Dry etching of Al interconnect lines is a critical technology for achieving high device densities. Reliable, reproducible etching of Al presents a number of challenges, as follows:

1. Al is always initially covered with a stable native oxide, Al_2O_3, which prevents etching until it is removed. The first step in the etch process is therefore a breakthrough of this oxide, either by Ar sputter etch or reagents that are strong reducing agents in plasma form. The Lewis acid BCl_3 works well for this application through the reaction



$$O + BCl_3 \rightarrow B - OCl + 2\,Cl$$

While CCl_4 also is an oxide reducing agent, it is not as effective at obtaining oxygen and water vapor in the reactor as is BCl_3 (33–35). This is a very important ability because moisture in the chamber from reactor desorption or resist erosion would react with the Al surface and create a new oxide that would inhibit further etching (36–38).
2. Resist erosion due to Cl attack, which is worsened by the presence of the etch product $AlCl_3$. In most cases, special chlorine-resistant resists are employed to reduce erosion.
3. Toxicity of the Cl_2-based gases and their products. These tend to dissolve and become concentrated in the vacuum pump oil, and precautions are necessary in changing and disposing of this oil. Further, oxidation of $AlCl_3$ or of the process oxides $SiCl_4$ and BCl_3 produces particulates that need to be filtered from the pump oil.
4. Hygroscopic nature of the etch byproducts $AlCl_3$. The presence of this species on the reactor walls will lead to absorption of moisture if the chamber is opened to air; this is minimized by use of vacuum load locks and keeping the reactor chamber walls at $\geq$35°C.
5. Presence of sidewall passivating $AlCl_3$ residues, which can react with moisture in the air upon removal of the wafer from the reactor, corroding the Al line by formation of HCl. Several methods are employed to overcome this, including rinsing in deionized water, in situ removal of resist with an O_2 plasma (which also replaces the $AlCl_3$ with Al_2O_3), and use of an F_2-based plasma to form AlF_3, followed by rinsing in HNO_3 to remove the fluoride and passivate the Al.
6. Difficulty in volatilizing Si and/or Cu additives to the Al (for improved electromigration resistance) (39). In particular, to remove Cu, either very high levels of ion bombardment or elevated substrate temperatures ($\geq$180°C) are necessary, requiring special hardening of the resist mask (40).

To achieve anisotropy in Al dry etching, it is always necessary to include a sidewall passivant, such as $SiCl_4$, CCl_4, $CHCl_3$, or BCl_3, usually in concert with a resist mask to produce a sidewall polymer. For example, BCl_3 will etch Al isotropically if a dielectric mask is used in place of resist, implicating the latter in the sidewall passivation mechanism. The strong chemical nature of Al etching makes it susceptible to loading effects, and with a small exposed area the etch rate and degree of undercut may be high.

ETCHING OF REFRACTORY METALS AND SILICIDES

Refractory metal silicides are increasingly replacing doped polysilicon in gate interconnects in MOS integrated circuits. For a number of device applications a polycide (polySi/silicide sandwich) involving $MoSi_2$, WSi_2, $TaSi_2$, or $TiSi_2$ layers is employed. In other cases the pure metal is used because it may have a much lower resistivity than the corresponding silicide, and it may be deposited by chemical vapor deposition (CVD), which produces superior step coverage to sputtering.

The chlorides of W and Mo have much lower vapor pressures than the corresponding fluorides, and thus the typical chemistries for etching are CF_4/O_2, SF_6, and so on. For Ti and Ta, the chloride etch products have higher or comparable vapor pressures to their fluoride counterparts. Ion bombardment is necessary in many cases to increase verticality of the pattern transfer, although TiW usually etches anisotropically because of the low volatilities of the tungsten chloride products (41–51). Since the silicides contain more than one element, it is necessary to have product desorption at similar rates to retain good surface morphology. For example, the vapor pressure of SiF_4 is several orders of magnitude larger than that of MoF_6, and therefore desorption of the latter is generally rate limiting during etching of $MoSi_2$. The desorption rates can be juggled by increased substrate temperature, lowered process pressure, or increased ion bombardment. It is somewhat unusual in Si technology to have a situation in which the rate-limiting step is evaporation of the reaction product, rather than surface reaction kinetics. Often, to improve anisotropy, refractory metal and polycide interconnects are etched with mixed halogen plasma chemistries to achieve high rates (at high F atom concentrations) and yet maintain some anisotropy through formation of chlorinated sidewalls. In general, the metals are less sensitive to undercutting than polysilicon. To avoid differential undercut in polycide structures, multistep etch regimes are often employed in which the refractory metal silicide is removed in a mixed halogen chemistry, followed by Cl_2/O_2 etching of the polysilicon. Tungsten and Mo can be etched in BCl_3/Cl_2 without undercut, but Ti is susceptible to isotropic sidewalls.

ETCHING OF PHOTORESIST AND POLYMERS

Removal of photoresist by "ashing" in an O_2 plasma to form CO_2, CO, and H_2O species was the first major application of plasma etching in microelectronics. Typical removal rates are around 1000 Å · min^{-1}, resulting in a 10 min process time for a standard 1 μm thick resist scheme. There is often a strong loading effect because a large number of wafers are cleaned at the same time; and because the process is then diffusion controlled, clearing of the resist begins from the perimeter of

the wafers and leads to a bullseye pattern during the removal. Eventually, of course, the entire film is cleared.

Directional etching for contact hole formation in polyimide dielectric layers, and pattern delineation in organic polymers, is also necessary and is generally carried out in O_2/CF_4 plasmas.

The absence of ion bombardment during photoresist stripping means there is no ion-induced damage (52–57). Moreover, the addition of a few percent CF_4 or SF_6 to the O_2 flow can substantially increase the resist removal rate. This appears to occur by F removing H from the resist as HF and leaving an alkyl that is very reactive with oxygen. The strip rates are as high at 1 $\mu m \cdot min^{-1}$ in O_2/CF_4, while elevating the sample temperature to 200°C and employing microwave excitation leads to even higher rates, 8 $\mu m \cdot min^{-1}$ (52).

Etching of resists and polymers is particularly important in bilevel lithography, which is employed to overcome step coverage problems in circuit topology. The scheme typically consists of an initial thick planarizing organic film, followed by a thin dielectric, metal (or semiconductor) layer, usually termed the transfer layer. The stack is completed with a thin imaging resist, which is lithographically patterned. An F_2-based dry etch is then used to transfer the pattern into the transfer layer, with reasonable selectivity over the underlying planarizing layer. The transfer layer material is then employed as the mask for O_2-based etching of the planarizing layer. The advantage of this process is that topology can be planarized using the thick polymer film, but the associated loss of resolution is overcome by using the second, thin imaging resist, which by itself would have insufficient thickness and etch resistance to be suitable.

Anisotropic etching of polymers in O_2-based plasma chemistries also involves sidewall passivation, generally by redeposition of SiO_2 from the mask, crosslinking of the immediate sidewall material, and backsputtered substrate material. Etch-back planarization of SiO_2 for defining patterns over high substrate topographies involves equirate etching of resist and oxide, generally in a well-calibrated CF_4/O_2 chemistry.

LOADING AND ASPECT-RATIO-DEPENDENT ETCHING

The loading effect refers to a decrease in etch rate with increasing exposed wafer area, due to a greater consumption of reagents (22). In principle it should be possible to explain these effects by noting the bulk diffusion-limited reagent supply. The practical effect of loading is that an adjustment of etching time must be made for each different amount of material (either wafers or exposed area). Depending on the gas phase mean free path, the effect may be both global and local.

The loading effect may be described by several different representations of the same equation:

$$R = \frac{R_0}{1 + kA}$$

where R_0 is the empty chamber etch rate, A is the area of exposed material to be etched, and k is a reactor-dependent constant

$$R_A = \frac{(K_E/K_L) \cdot G}{1 + (K_E \rho A / K_L V)}$$

where R_A is the etch rate at area A, G is the rate of production of etchant species, ρ is the number density of substrate molecules, V is the reactor volume, and K_E and K_L are rate constants for etching and etchant loss in an empty reactor. For a large wafer load this relationship simplifies to

$$R_A = \frac{GV}{\rho A}$$

and the etch rate is inversely dependent on wafer load area A. The loading effect may be reduced by making K_L large relative to K_E by processes such as high flow rate (rapid pumping) that consume etchant species.

Ideally the etching should be independent of feature size, aspect ratio, fraction of exposed material, and mask material. While the loading effect is severe in isotropic etch processes where etch rate is proportional to etchant species, it is generally smaller in anisotropic etching because in the latter case etch rate is mainly controlled by ion bombardment flux. The local or microscopic loading effect occurs when there is sensitivity of etch rate to pattern density, and thus etch rates may change over distances of microns. The reactant concentration varies locally due to consumption by a reactive material and nonconsumption by a nonreactive material. What this means practically when etching Si through to an underlying layer such as SiO_2 is that an increased overetch time is required to ensure clearing of Si from the slower etching regions, and thus there is a more severe demand on selectivity. In addition, this overetch solution is not possible for trench etching in single-crystal Si.

Another practical result of the loading effect is in etching of Al interconnect lines. In some conditions the Al etch rate will increase as the Al film clears and undercutting will proceed very quickly if the plasma exposure is continued.

The aspect ratio dependence of etch rate will become increasingly more of an issue as trench widths decrease while at the same time having even greater depths. In general, the etch rate decreases almost linearly as the aspect ratio increases and is essentially independent of trench diameter opening. A number of mechanisms have been postulated for this effect, including diffusion problems with the supply of reagent to the bottom of the trench, consumption of reactant at the trench sidewalls, and presence of developing electric fields within the trench (4).

DAMAGE AND RESIDUES

Substrate and oxide damage and the presence of etch residues are all deleterious effects of dry etching (58–63). Typical ion energies range from 50 to 700 eV at fluxes around 10^{15} ions $\cdot$ cm^{-2}, and this can produce ion bombardment damage. Additionally, particulate formation from the gas phase and sputtering of metallic impurities from reactor surfaces are problems. Since etch anisotropy occurs due to ion bombardment and deposition of polymeric layers, it is inevitable that lattice damage and surface (or sidewall) disruption will be present. A typical Si surface after reactive ion etching (RIE) may consist of a teflonlike polymeric film typically 30 Å thick, followed by a 20 Å Si- and O-rich interfacial polymer, followed by ~30 Å of heavily damaged Si, followed by up to 250 Å of Si-containing hydrogen, if the latter was part of the etch chemistry.

The organic top film is readily stripped in an O_2 plasma, while annealing at 400°C is generally sufficient to anneal out lattice disorder. This anneal should also remove the effects of hydrogen passivation of boron dopant impurities.

In photoresist stripping there is generally a residue of alkali ions and heavy metals that were present in the resist itself (2). These must be removed by net chemical cleaning to prevent their incorporation into oxide or the Si itself during subsequent processing.

Accumulation of charge in the gate area of MOS transistors may seriously degrade device performance and occurs during plasma processing when a wet current is drawn through a wafer containing floating gates (63). This may produce field-induced breakdown of the gate oxide.

In general, RIE damage is used to refer to any or all of the following phenomena (58,59): surface residues, especially fluorocarbon films, lattice displacement damage consisting of point defect complexes, hydrogen passivation of dopants, impurity implantation, heavy metal contamination by sputtering of electrode or other reactor materials, mobile ion contamination, surface roughness from micromasking and redeposition, gate oxide breakdown due to change, and post-etch corrosion by Cl_2 residues, especially on Al.

A particular feature concerning the effect of surface residues on morphology of etched Si is the appearance of so-called black silicon after Cl_2 trench etching; this consists of grasslike or more isolated surface features resulting from contamination or oxide precipitates that produce micromasking.

PLASMA ANALYTICAL TECHNIQUES

There are a large number of endpoint detection, plasma diagnostic, and plasma analytical techniques available, and here we will summarize just a few. For detection of the end of an etch process, laser interferometry optical emission spectroscopy and mass spectroscopy are the most common methods.

1. *Optical Emission Spectroscopy.* Most processing plasmas emit radiation from the infrared (IR) to ultraviolet (UV) regions of the spectrum, and the intensity of these emissions as a function of wavelength can be measured with a spectrometer. Quantitative concentrations of different species giving rise to the peaks can be obtained if the observed intensities are calibrated against those of a small amount of gas such as Ar added for that purpose. This is known as actinometry (64–68). Table 3 lists some common emission lines used for endpoint detection (3,4).
2. *Mass Spectrometry.* A differentially pumped mass spectrometer unit attached to a reactor can sample constituents of the gas with an electron beam to ionize them and then measure the mass spectrum. One must be aware of the presence of molecule fragmentation. For example, a CF_2^+ ion might originate from the CF_2 radical, but could also come from the molecules CHF_3 and C_2F_4. Due to difficulties in assigning peaks due to species with the same mass-to-charge ration (e.g., Si^+, CCO^+, $C_2H_4^+$, N_2^+, Fe^{2+}) and the fact that the reactive plasma eventually degrades the filament in the mass filter, mass spectrometry is generally not used for endpoint detection.

Table 3. Common Optical Emission Lines Used for Endpoint Detection

Material	Etchant Gas	Emitting Species	Wavelength (nm)
Silicon	CF_4/O_2; SF_6	F (Etchant)	704
	CF_4/O_2; SF_6	SiF (Product)	440; 777
	Cl_2; CCl_4	SiCl (Product)	287
SiO_2	CHF_3	CO (Product)	484
Si_3N_4	CF_4/O_2	N_2 (Product)	337, 452–650
	CF_4/O_2	CN (Product)	387
	CF_4/O_2	N (Product)	674
W	CF_4/O_2	F (Etchant)	704
Al	CCl_4; Cl_2; BCl_3	Al (Product)	391; 394; 396
	CCl_4; Cl_2; BCl_3	AlCl (Product)	261
Resist	O_2	O (Etchant)	777; 843
	O_2	CO (Product)	484, 450
	O_2	OH (Product)	309
	O_2	H (Product)	656

3. *Laser Reflectance and Interferometry.* This monitors changes in film thickness thorugh changes in the reflectance as it is being etched. It therefore gives an accurate measure of etch rates in real time and requires only that the film be partially transparent and that the film and substrate have different optical constants (69,70). The spacing between adjacent maxima in the reflected beam is equal to $\lambda/2n$, where λ is the wavelength of the laser light and n the refractive index of the film. The main drawbacks of this technique are the requirement for a special test area on the wafer and the fact that etch rate is only sampled in this area.
4. *Langmuir Probes.* A conducting metal probe smaller than the particle mean free path placed directly in the plasma can be used to measure electron density, temperature, and plasma potential from the current-voltage characteristic. An extensive literature exits on probe theory and operation (71–73), but there are numerous pitfalls to their use, including the fact they do not work well in the sheath region of the plasma and they can disturb the electron temperature.

Other techniques for plasma diagnosis include optogalvanic spectroscopy, where a change in discharge parameters induced by the absorption of light is monitored (74,75); laser-induced fluorescence, where a tunable dye laser excites species and the emission spectra is measured (77); and ellipsometry.

COMPOUND SEMICONDUCTOR ETCHING

There are four main etch techniques employed in compound semiconductor etching:

1. Simple Ar^+ ion milling at energies of ~500 eV for formation of shallow mesa isolation for field effect transistors (FET)
2. Chemically assisted ion beam milling, where Cl_2 gas is injected from a nozzle near the sample and a separate plasma source provides Ar^+ ion bombardment

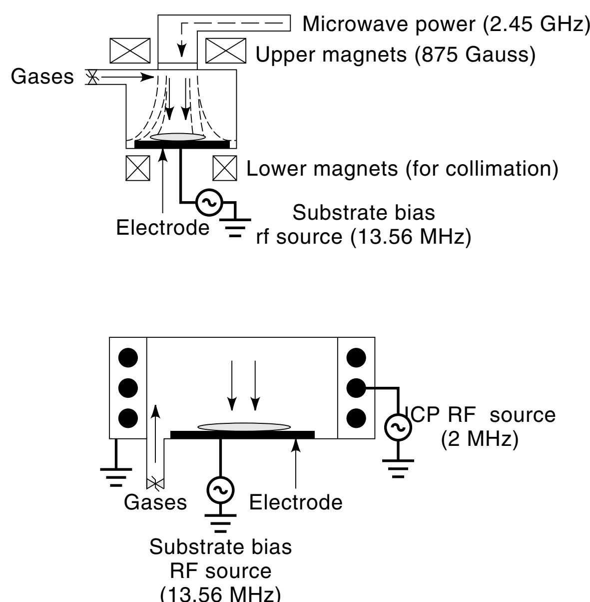
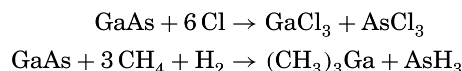


Figure 2. Schematic of Electron cyclotron resonance (top) and inductively coupled plasma (bottom) reactors.

3. RIE, similar to that used in Si technology, which is employed for applications ranging from gate mesa formation on heterostructure FETs (etch depth ~300 Å, but high selectivity, >600, required for GaAs over AlGaAs) to through-wafer via creation for power FETs (etch depth ~100 μm)
4. High-density etch reactors, principally electron cyclotron resonance (ECR) and inductively coupled plasma (ICP), which have ion densities several orders of magnitude greater than RIE systems and produce much higher etch rates at lower ion energies. Schematics are shown in Fig. 2.

The typical gas chemistries for III–V semiconductors are listed in Table 4—note that F_2-based gases do not create volatile etch products, which is an advantage in the sense that dielectric films are easily patterned with high selectivity over the underlying semiconductor. Typical overall etch reactions for Cl_2 or CH_4/H_2 plasma etching of GaAs follow:



$$GaAs + 6\,Cl \rightarrow GaCl_3 + AsCl_3$$
$$GaAs + 3\,CH_4 + H_2 \rightarrow (CH_3)_3Ga + AsH_3$$

In practice the Cl_2 etch products depend on the chlorine pressure, etch temperature, and ion flux. Chlorine molecules and atoms do not etch GaAs at temperatures below several hundred degrees in the absence of ion bombardment, but desorption of subchlorine and fully chlorinated species occurs at room temperature when ions are present. Indeed virtually all etching of compound semiconductors occurs by ion assistance.

Table 5 shows some boiling points for III–V etch products. Note that Cl_2 is a good choice for most materials, with the exception of InP, where the $InCl_3$ product is relatively involatile at normal temperatures. To enhance desorption it is necessary either to heat the InP substrate during the etch process or employ a high ion flux to assist removal of the $InCl_3$. At low pressure (<20 mtorr) the etching is relatively anisotropic for all III–V semiconductors because of the ion-driven nature of most of the processes (78).

Damage in dry etched compound semiconductors consists generally either of ion-induced deep-level compensation, which degrades both the electrical and optical quality of the material, or of stoichiometry changes to the near surface through preferential loss of one of the lattice elements. Damage induced by ions is proportional to the flux-energy product, and therefore in high-density etch systems the ion energy must be kept low to minimize creation of deep-level states (78,79).

Table 4. Typical Etch Mixtures for III–V Semiconductors

Chemistry	Comments	Typical Rates
(a) Cl_2 based		
Cl_2, $SiCl_4$, BCl_3, CCl_2F_2	Usually have additions of Ar or He. Smooth for GaAs, rough for InP.	3000 Å · min^{-1} for GaAs; 300 Å · min^{-1} for InP
(b) CH_4/H_2 based		
CH_4/H_2, C_2H_6/H_2 C_3H_8/H_2, CH_4/He	Ar often added for stability. Smooth etching of InP. Heavy polymer deposition.	300 Å · min^{-1} for InP and InGaAs, lower for GaAs
(c) I_2 based		
HI, CH_3I, C_2H_5I, I_2	High rates at room temperature for InP. Corrosive. No polymer deposition.	5000 Å · min^{-1} for InP and InGaAs; 3000 Å · min^{-1} for GaAs
(d) Br_2 based		
HBr, CF_3Br, Br_2	Corrosive	600 Å · min^{-1} for GaAs; 400 Å · min^{-1} for InP

Table 5. Boiling Points of III–V Etch Products

Species	Boiling Point (°C)
$GaCl_3$	201
$GaBr_3$	279
GaI_3	Sub 345
$(CH_3)Ga$	55.7
$InCl_3$	600
$InBr_3$	>600
InI_3	210
$(CH_3)_3In$	134
$AlCl_3$	183
$AlBr_3$	263
AlI_3	191
$(CH_3)_3Al$	126
NCl_3	<71
NI_3	Explodes
NF_3	−129
NH_3	−33
N_2	−196
$(CH_3)_3N$	2.9
PCl_3	76
PBr_5	106
PH_3	−88
$AsCl_3$	130
$AsBr_3$	221
AsH_3	−55
AsF_3	−63

High-density reactors are particularly useful for patterning of materials with high bond energies, such as GaN, AlN, and InN, which form a particularly attractive alloy system for photonic devices ranging from the red-UV regions of the spectrum. While the etch products for these materials are just as volatile as for more conventional semiconductors such as GaAs, etch rates under RIE conditions are generally factors of 5 to 10 lower because of the low rate of bond breaking. In the much higher ion fluxes available with ECR or ICP reactors, it is easier to break bonds that will allow the etch products to form, and therefore much higher rates are obtained.

To achieve smooth etched surface morphology on compound semiconductors, there are several necessary conditions that must be met. First, the native oxide should be removed quickly at the start of the etch process—if it breaks through nonuniformly, this roughness will be replicated in the etched semiconductor surface. Plasma chemistries involving BCl_3 or CH_4/H_2 readily attack the native oxide. Second, there must be equirate removal of both the group III and group V elements, and this can only be achieved by adjusting the ion/neutral ratio and ion flux and energy, since generally the etch products for these elements have different volatilities. Third, both the mask material and carrier wafer (electrode materials may have a strong influence on etched surface morphology through effects such as micromasking or altering the ion/neutral balance).

The same basic plasma chemistries are employed for II–VI compound semiconductors such as ZnSe, SnS, CdS, and HgCdTe. These materials are generally even more susceptible to preferential loss of one of the constituent elements than the III–V materials, but can be etched smoothly and anisotropically in Cl_2- or CH_4/H_2-based plasma chemistries. For materials such as SiC, which has an extremely high bond strength, high flux reactors produce much higher etch rates than conventional RIE. It appears that fluorine-based plasma chemistries such as NF_3/O_2 and SF_6/Ar provide the highest etch rates, with Cl_2, Br_2, and I_2 chemistries being less efficient. Once again, it is necessary to adjust the plasma conditions to avoid preferential loss of C from the near surface.

Essentially any material can be etched either in Cl_2- or F_2-based plasmas, with additional ion bombardment, allowing magnetic, display, or insulators to be patterned for device applications.

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PLASMA CHEMISTRY. See Passivation.