Plasma Etching

An Introduction

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will have a rate law that is second or third order, $r = k_2 n_{CF_2}^2$ ($\propto P^2$) (it will be third order at pressures where M appears in the rate expression). Similarly, the effective kinetics of sequential reactions leading to growth of trimers (C_3F_6) in this example would be still higher order [42]. This is symptomatic of a general tendency to favor oligomer and polymer growth relative to etching, when the pressure increases in a fixed mixture containing F atoms and CF_2 radicals. Similarly, with decreasing pressure, the etching rate in this simplified example will rise relative to the rate of oligomer and film formation.

Increasing pressure and decreasing temperatures increase the surface concentration of physisorbed species according to their adsorption isotherms, and chemical etching rates increase in step with the surface concentration of etchant. While adsorption effects in plasma etching have not been studied, in the closely related low pressure gaseous etching (LPGE) [46, 47] they can lead to an apparent "negative activation energy." Interesting conditions were found in which decreasing temperature led to an increase in the rate of silicon etching by XeF_2, ClF_3 and other interhalogen compounds, apparently because the surface concentration of active species increased faster than the decline in rate constant with temperature [46, 47] (see Section III.1).

Finally, we note that at fixed composition and mass flow rate, the ratio of convective relative to diffusive mass transport (e.g., the Peclet number), is constant and both are independent of pressure. Therefore the ratio of mass transport rates relative to first order surface reactions will vary as $1/P$ so that lower pressure tends to overcome local reactant depletion, or mass transport limitations in chemical reaction.

E. TEMPERATURE EFFECTS

Temperature, like pressure, has a profound influence on discharge chemistry. To be clear, we really should distinguish between gas and surface temperatures. However, the gas temperature is a complex function of local power input, heat transfer and transport phenomena. Only the surface temperature is really controllable. Moreover, for the pressure and flow conditions generally encountered in low pressure plasma etching, the thermal boundary layer (e.g., the distance from the surface over which heat transfer maintains the gas close to wall temperature) is much thicker than a mean-free path, so impinging gas species are already at the surface temperature.

In our discussion of kinetics, we said that the rate constants for chemical reactions are a function of temperature. Thus temperature has a dominant

effect on selectivity, etch rates and the degradation of resist masks. As we shall see, the morphology of etched surfaces is also greatly affected by temperature. Finally, physisorption and diffusion are sensitive to temperature, although these topics are beyond the scope of this chapter.

1. Effect of Temperature on Rate Constants

The rate constants for elementary chemical reactions usually vary with temperature according to the Arrhenius expression,

$$k(T) = A(T)e^{-E_A/RT}, \tag{31}$$

where A is a "pre-exponential" which is weakly dependent on temperature, and E_A is the "activation energy." The activation energy is the height of the energy barrier that reactants must overcome to approach each other and combine, (or the energy barrier for dissociation in the case of a single decomposing reactant). The exponential term is known as an "Arrhenius factor." As an example of this behavior, the etch rates for fluorine atoms etching silicon and SiO_2 are in excellent agreement with the expression

$$\text{Etch Rate} = Cn_F T^{1/2} e^{-E_A/RT} \ \text{Å/min}, \tag{32}$$

where the constants, C and E_A for Si and SiO_2 etching are shown in Table 4. Unlike the expression for the *rate constant*, Eqn. 31, the *reaction rate* Eqn. 32 depends on a concentration (n_F) as given by Eqn. 27. The weak pre-exponential $T^{1/2}$ dependence can be understood as follows: The flux of F atoms to a surface is $n_F v_F/4$ (see Chapter 1), which is proportional to $T^{-1/2}$ since n_F is inversely proportional to T according to the perfect gas

Table 4 Preexponential factors and activation energy for F atom etching of Si and SiO_2. The rate equation is ER (Å/min) $= An_F T^{1/2} e^{-E_A/RT}$.

FILM	A	E_A (kcal/mole)	RATE Å/min (298 K, $n_F = 3 \times 10^{15}$ cm^{-3})
Si	2.86×10^{-12}	2.48	2250
SiO_2	0.614×10^{-12}	3.76	55

$ER(\text{Si})/ER(\text{SiO}_2) = 4.66\, e^{1.27/RT}$
$= 44$ (at 298 K)

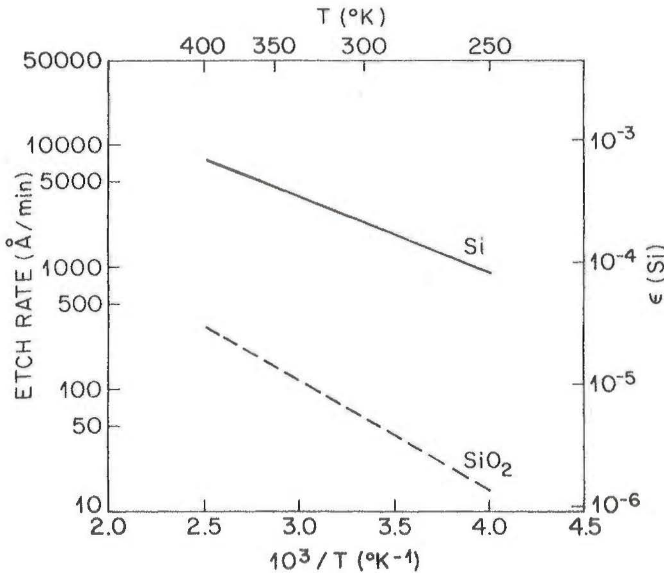

FIGURE 9. Arrhenius plot of silicon and SiO_2 etch rates, and Si reaction probability with F-atoms. The logarithms of these parameters are a linear function of $1/T$. The etch rates shown are based on a plasma F-atom concentration of 3×10^{15} cm^{-3}. Note that the reaction probability, ϵ is defined here as the probability that an impinging silicon atom leaves the surface as a silicon fluoride product (no particular product stoichiometry is assumed). Since conflicting definitions of ϵ appear in the literature, published values should be interpreted with caution.

law, and v_F is proportional to $T^{1/2}$. Hence, if the probability of an atom reacting once it is on the surface is proportional to the Arrhenius factor, the reaction rate will have the dependence shown. The logarithms of the silicon etch rate and probability of an atom reacting when it reaches a silicon surface are plotted against $1/T$ in Fig. 9. A straight line in these semilogarithmic coordinates indicates an Arrhenius dependence, and the slope of the line gives E_A. The weak $T^{1/2}$ factor has almost no effect on the slope in these coordinates.

Incidently, the final silicon-containing product of both Si and SiO_2 etching in F–containing discharges is SiF_4. The reaction rates in Table 4 belong to initial reactions between F atoms and the substrates which form intermediate species, not the final product. But they *are* also the etch rates, because the initial step is the slowest *rate determining* reaction. That is, the rate of sequential reactions is determined by the slowest step.

Since F atom etching rates of both Si and SiO_2 conform to exponential Arrhenius behavior, the selectivity, which is their ratio, is exponential in

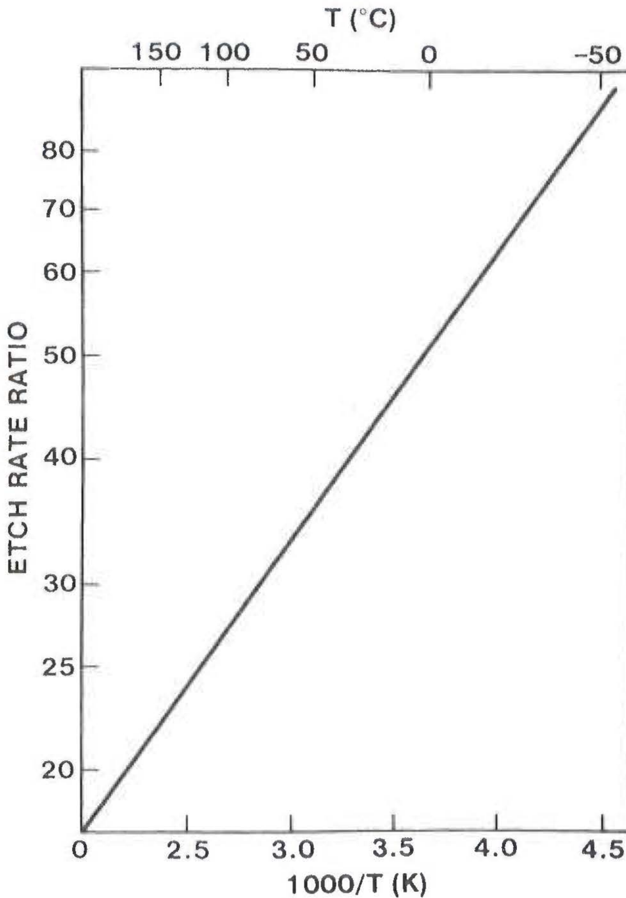

FIGURE 10. Selectivity for etching Si over SiO_2 as a function of $1/T$. The decline of selectivity with temperature is an effect of the Arrhenius dependence.

$1/T$ as well. Figure 10 shows the selectivity for etching Si relative to SiO_2 as a function of $1/T$. At room temperature, selectivity is about 44 : 1, but if the plasma heats the substrate, the selectivity will fall. Conversely, higher selectivity can be achieved by cooling the substrates to below room temperature. Notice also that these exponential factors, $\exp^{-E_A/RT}$, always approach unity when RT is much larger than E_A. Selectivities decrease with temperature and approach the ratio of the Arrhenius pre-exponential factors—in this case 4.7 : 1. Surface temperature is an essential variable.

As we will see, this example is more than an academic exercise. F atoms, made from a variety of feed gases, are widely used to etch Si, SiO_2 and

Si_3N_4. This is usually done by the purely chemical reactions discussed here, but anisotropic etching of SiO_2 with F atoms is also possible, as described in Section IX. To study the ideal etching reactions, substrates were exposed to dissociated F_2 from a discharge in a temperature-controlled cell. However, F_2 is considered too hazardous for process application so other sources of F atoms, including NF_3, mixtures of CF_4, C_2F_6 etc. with O_2, and SF_6/O_2 are used industrially. The choice between these alternatives is made on the basis of economics and side effects on the etching process. The plasma chemistry of halocarbon/oxygen mixtures is important in a rich variety of etching processes and will be discussed in Section IV.

While discussing Si etching by F atoms, we should point out that certain gaseous fluorine-bearing compounds will react even without a plasma. XeF_2 is probably the best known of these substances, and investigators have repeatedly claimed that its reaction with Si follows the same basic mechanisms as F atoms etching. This claim has, however, been repeatedly discredited. Several investigators have shown that the reactivity, the rate, the intermediates, and the temperature dependence of XeF_2 etching silicon and SiO_2 are quite different from F atoms etching. Apparently, the main reason XeF_2 has been used in so many studies is that it is commercially available (in a bottle) and stable. Measuring its reactions doesn't require the techniques that are necessary for F atom studies.

In fact, XeF_2 is but one of a family of "plasmaless" low pressure gaseous etchants (LPGE) that can be used to etch silicon selectively, making SiF_4 as a product. Other gases of this type are listed in Table 5, where atomic fluorine is included for comparison. Notice that the room temperature etch rates and apparent activation energies vary widely, consistent with the

Table 5 Reaction rates for LPGE etching of Si by various gases (at room temperature; * means not measured).

Reactant	E_a Kcal/mole	Etch Rate Å/min-Torr
XeF_2	6.1	230,000
BrF_3	*	50,000
F	2.5	9,200
IF_5	2.5	2,200
BrF_5	*	1,500
ClF_3	4.1	1,200
ClF	*	< 2
F_2	9.2	0.3

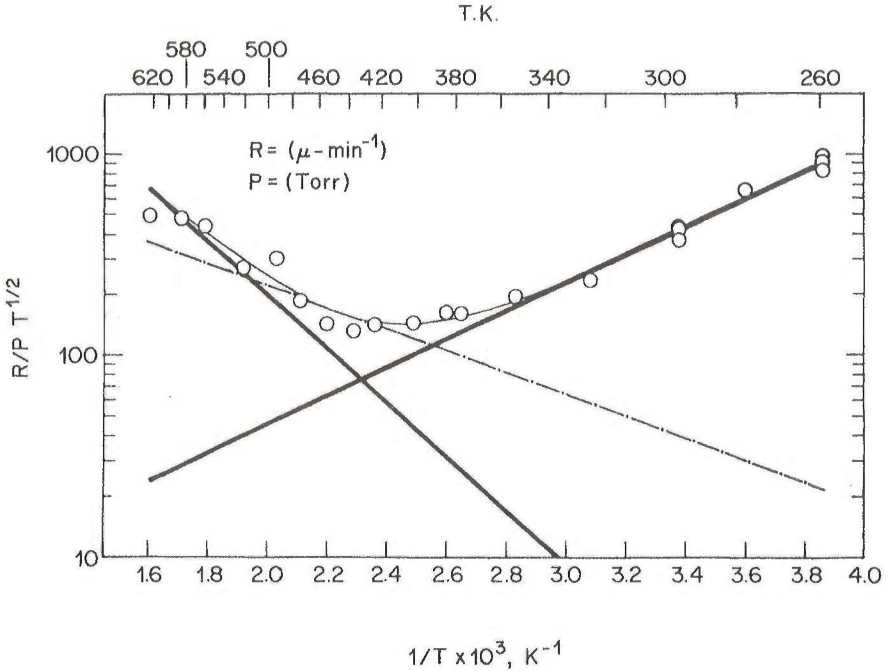

FIGURE 11. Etch rate of (100) silicon by XeF_2 as a function of temperature (upper curve and data points). The thick solid lines are asymptotes showing a normal Arrhenius behavior at high temperature (negative slope) and anomalous positive slope at low temperature which is attributed to adsorption control. For comparison, the etch rate by an equivalent pressure of F atoms is shown by the lower line (—•—•).

diverse chemical nature of these etchants. Unlike atomic fluorine, none of the plasmaless etchants attack SiO_2 at all—at least within the several hundred degree temperature range in which they have been studied. Another interesting aspect of their behavior is that many of them exhibit a "counter-Arrhenius" behavior at low temperature. Figure 11 shows this peculiarity for XeF_2, which contrasts with the temperature dependence of F atom etching. It is believed that the increasing etch rate with decreasing temperature means that adsorption of XeF_2 on the surface is rate-limiting—that is, an increase in the surface concentration of XeF_2 with falling temperature more than compensates for a decrease in the reactivity. Another way of saying this is that the concentration, n_A, in Eqn. 27 should really be a surface concentration, and that as temperature drops (below the minimum in the curve), adsorption makes the surface concentration rise faster than the rate, $k(T)$, falls.