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REACTIONS of XEF_2, FLUORINE ATOMS AND MOLECULAR FLUORINE WITH SILICON AND SIO_2 SURFACES

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ABSTRACT

Silicon gasification by XeF_2 is compared with F-atom etching under conditions typical of those used in plasma etching. Temperatures ranged from -15 °C to 360 °C and XeF_2 pressures were between 0.05 Torr and 2 Torr. Silicon etching by XeF_2 shows a sharply different etch-rate/temperature dependence than the Si/F or Si/F_2 reaction systems; there is no detectible reaction between XeF_2 and SiO_2 in contrast to the F-atom/SiO_2 system. Etch rates for XeF_2 increase sub-linearly with pressure greater than or equal to 0.5 Torr, also in contrast to analogous F-atom reactions. These data indicate that physisorption can limit silicon etching by XeF_2 and show that basic studies which use XeF_2 as a compound for modeling the etching of silicon and SiO_2 by F-atoms should be interpreted with caution since these two reagants do not exhibit similar behavior.

INTRODUCTION

Fluorine-containing gases and gas mixtures have been widely used for plasma etching silicon and its compounds. Fluorine atoms are the main or sole silicon etchant in many plasmas and consequently the reactions of atomic fluorine with Si[1,2] and SiO_2[3] have been studied in some detail. Several researchers have proposed that XeF_2 reactions with Si and SiO_2 are essentially the same as those of F-atoms. Thus XeF_2 has been extensively used as a model compound in research on the basic mechanisms of plasma etching.

The assumption that silicon attack by XeF_2 behaves the same as its interactions with F-atoms has been applied to isotropic etching[4,5] and to ion-stimulated high vacuum beam studies[5,6,7]. It was apparently based on three observations: (1) XeF_2, like F-atoms, rapidly and spontaneously etched silicon[4], (2) Xe was not detected on the silicon surfaces in high vacuum Auger[4,8] and XPS[8] measurements and (3) chemisorbed fluoro-silicon species are efficiently gasified by ion bombardment. Although there was evidence of a wide disparity between the spontaneous reaction rate of XeF_2 with silicon and comparable etch rates of atomic fluorine[9], the significance of this comparison was uncertain because the F-atom[1] and XeF_2 data[4,5] were taken under drastically different conditions.

Similarly, F and XeF_2 reactions with SiO_2 were believed equivalent. Early data showed that XeF_2 did not etch SiO_2 and it was assumed that the same result would apply to the reaction of F-atoms with SiO_2[6]. Subsequently when experiment showed that F-atoms spontaneously etch SiO_2, it was suggested that the measurements of XeF_2 interacting with SiO_2 may have been too insensitive to detect etching[10], or that the apparent discrepancy might be explainable in terms of flux differences[11].

We report the interaction of XeF_2 with Si and SiO_2, under the same circumstances previously used to investigate the kinetics of F-atom/Si and F_2/Si reactions. The data show that XeF_2 is a poor analog for silicon etching by fluorine atoms under plasma etching conditions.

EXPERIMENTAL

The reactive flow apparatus used in this study was similar to that used in our previous F-atom studies[1]. Oxide-masked silicon samples were bonded to the end of a 2.54 cm o.d. hard-coat anodized aluminum rod and positioned in-line with the wall of a 2.54 cm i.d. aluminum reaction cell. The reaction cell had five ports through which inlet and outlet tubes, a sapphire window, and the substrate holder were sealed with Viton or Kalrez o-rings. Part of the substrate holder that extended out of the reaction cell (22 cm) was heated electrically or cooled with a constant temperature bath to the desired temperature, while the rest of the cell was thermally insulated. A type-J thermocouple was inserted into a thermowell just under the sample to monitor substrate temperature which was varied between -17 and 360 °C. Pressures, between 0.05 and 2 Torr, were measured at the outlet of the reaction cell with a 10 Torr MKS capacitance manometer.

Chemiluminescence, originating in the gas phase above the silicon samples, could be monitored through a 1 cm diameter sapphire window which faced the sample surface perpendicular to the flow-tube axis. A photomultiplier tube, equipped with a 350 nm long pass filter and lenses, was used to measure the broad band emission. Emission spectra were also monitored with an optical multichannel analyzer (OMA) to compare them with the spectra from F and F_2 etching[2,12,13].

N-type (100) silicon wafers were patterned in a "checkerboard" arrangement of 10 KÅ thick oxide squares (5 mm per side) bounded by 285 μ wide Si stripes. Square samples ($\approx$ 3x3 mm) were cleaved from the wafers, with 2 to 3 mm^2 of exposed Si. Etch rates were determined from the etch depth divided by etching time. Chemiluminescent emission was monitored to detect any induction period in etching caused by oxide or contaminant clearing during the initial stages of reaction. So long as the native oxide was removed and the sample was etched immediately afterwards, no induction period was observed. In contrast, *no* etching was observed when the native oxide remained. This suggests little or no etching of the oxide occurs, as confirmed by oxide thickness measurements (below).

RESULTS AND DISCUSSSION

Etch rates, measured as a function of substrate temperature below $\approx$ 0.5 Torr, were fit to a general form of the Arrhenius equation

$$R_{XeF_2}(Si) = \nu_o \, n_{XeF_2} \, T^{1/2} \exp[-E/kT] \quad . \tag{1}$$

This can be written more explicitly as

$$\frac{R}{P} T^{1/2} = 9.65 \times 10^{18} \, \nu_o \exp[-E/kT] \tag{2}$$

where R is the etch rate of Si in $\mu-\text{min}^{-1}$, P is the pressure of XeF_2 in Torr, T is the substrate temperature (°K), E is the effective activation energy of the etching reaction ($\text{kcal}-\text{mole}^{-1}$), ν_o is a pre-exponential factor and k is the Boltzmann constant. In converting from Eq. (1) to Eq. (2), we have made the assumption that the gas temperature and the substrate temperature are equal, since at these pressures the gaseous boundary layer above the sample is thick and should be thermally equilibrated with the substrate.

In sharp contrast to previous studies of F-atoms etching silicon, Fig. 1 shows that an Arrhenius plot of the XeF_2 etch rate data (open circles) exhibits a complex behavior. Below 450 °K the etch rate decreases with increasing temperature; between 360 °K and 450 °K it reaches a minimum; and finally at higher temperatures it increases. Below 360 °K the Arrhenius plot is linear (bold line, positive slope) with a slope corresponding to an apparent *negative* activation energy of -3.2 kcal−mole^{-1}. The corresponding rate equation for the low temperature asymptote is

$$R_l(XeF_2) = 1.90\times10^{-19}\, n_{XeF_2}\, T^{1/2} \exp[3.2/kT] \quad \mu-\mathrm{min}^{-1} \ . \tag{3}$$

The characteristics of XeF_2 etching Si are completely different from the reactions with F-atoms[1] or F_2[13]. The rate of reaction between Si and F-atoms increases exponentially with temperature, as shown by the dot-dashed line in Fig. 1, and has an activation energy of 2.5 kcal−mole^{-1}. F_2, which etches Si with a lower probability than F-atoms, also displays an Arrhenius dependence on temperature, and has a higher activation energy: $E = 9.2$ kcal−mole^{-1}. Although the F-atom and XeF_2 rates are equal near the minimum (XeF_2 etch-rate versus T^{-1}) in Fig. 1 (≈ 410 °K), the XeF_2 etch rate is up to 40-fold greater elsewhere. The indicated linearity between etch rate and n_{XeF_2} was confirmed for several isotherms below ≈ 0.5 Torr, but fails at or above this pressure. The contrast between XeF_2 and F-atom reactions is even more striking for SiO_2. After one hour at 300 °C and 2 Torr XeF_2 there is no detectible etching (< 1 Å−min^{-1}−Torr^{-1} of SiO_2 [steam grown oxide on silicon]).

The XeF_2 etch-rate/temperature dependence in Fig. 1 suggests two different rate-limiting mechanisms, depending on the substrate temperature. The weak, but negative temperature dependence at low temperatures suggests that weakly adsorbed XeF_2 is the precursor to etching. This layer would be depopulated as temperature is increased at constant pressure. The isothermal etch rate increases with increasing pressure of XeF_2 in this region.

XeF_2 etches Si up to forty times faster than F-atoms at low temperature, even though it has more steric constraints because of its larger size. We attribute this to the weakly bound layer that allows a longer residence time for dissociation on the surface (e.g., the long residence time more than compensates for the exponential factor in the etch rate). This is consistent with the fact that XeF_2 is more polarizable than F-atoms or F_2 molecules, so that it should have larger heats of physisorption and condensation. Although the first bond dissociation energy of XeF_2[14] (54-58 kcal−mole^{-1}) is larger than the bond dissociation energy of F_2 (37 kcal−mole^{-1}), bond distortion would be larger for XeF_2 in a physisorbed layer, leading to more efficient dissociative chemisorption.

Evidently another reaction step dominates the reaction mechanism at temperatures above the rate minimum in Fig. 1 which may be *direct* dissociative adsorption of XeF_2 on a mixture of SiF_x ($0 \le x \le 2$). The activation energy in this region is larger than that for F-atoms. Assuming that this high temperature reaction does not contribute significantly at low temperature, the asymptotic slopes can be assigned to each of these two mechanisms and the rates separated. The high temperature asymptote (Fig. 1, bold line, negative slope) is obtained by subtracting the low temperature line from the overall rate above 380 °K and exhibits an activation energy of 6.1 kcal−mole^{-1}. The rate equation for this high temperature asymptote is

$$R_h(XeF_2) = 9.26\times10^{-15}\, n_{XeF_2}\, T^{1/2} \exp[-6.1/kT] \quad \mu-\mathrm{min}^{-1} \ . \tag{4}$$

The smooth curve through the data corresponds to the sum of Eqs. (3) and (4).

From these results it is clear that the reactions of XeF_2 and F-atoms with Si are governed by different rate-limiting steps. Most likely the elementary rate-limiting steps for XeF_2 at room temperature involve dissociative chemisorption, and/or diffusion to sites that allow dissociation. The rates of these steps are probably sensitive to surface coverage (which may be constant as a saturated SiF_2 layer[9]), steric constraints on the orientation of a XeF_2 molecule which dissociates at a site, and the density of defects in the SiF_2 layer. By contrast, the temperature dependence of the F-atom/silicon reaction and accompanying chemiluminescence suggest one dominant kinetic limitation.

The dependence of reaction rate on pressure at 296 °K and 558 °K (which have almost equal $\frac{R}{P}T^{1/2}$ exponential terms at low pressures in Fig. 1) were measured. At both temperatures the reaction rate increases linearly with pressure until 0.2 Torr, but increases sublinearly for pressures greater than or equal to 0.5 Torr. Although both reaction regimes exhibit a similar sublinear pressure dependence they probably are dominated by different mechanisms, as postulated above. In both cases adsorption may govern the kinetic limitation at high pressure.

This simple mechanism provides a phenomenological understanding of the data and the role of XeF_2 adsorption in both temperature regimes; however, more experimentation would be needed to quantify these results and verify the proposed mechanisms. Note that this XeF_2 study is in sharp contrast with our F-atom studies where low secondary surface coverage is maintained across the range of temperature and pressure. Moreover, the rate equations (3) and (4) show some agreement with data from other studies done under totally different conditions. For instance if the low coverage $R_h(XeF_2)$ [Eq. (4)] is extrapolated to 50 °C, the reaction probability is 2×10^{-4} Si atoms removed per incident XeF_2. This is in good agreement with the $4-14\times10^{-4}$ observed by Vasile at this temperature[15] using low XeF_2 fluxes (0.01 $ML\text{-}sec^{-1}$) and coverage (we have multiplied Vasile's reaction probabilities[15] for unsputtered Si(100) by two to convert them to our basis). Similarly the asymptote $R_l(XeF_2)$ at 300 °K corresponds to a probability of 0.013, which compares favorably with the value of 0.01 - 0.025 obtained by Winters and Coburn[4] in the pressure regime 4×10^{-4} to 1.4×10^{-2} Torr. We therefore postulate that physisorption might have had a significant effect on rates observed at these intermediate pressures.

The present interpretation seems to disagree with Auger[4,8] and XPS[8] measurements taken at low pressure, which show no Xe present on Si and SiO_2 surfaces. The absence of Xe and the presence of fluorine, on both Si and SiO_2 surfaces after XeF_2 exposure has been interpreted to mean that XeF_2 merely delivers F to the surface (molecular XeF_2 does not have any appreciable lifetime on the surface) so F and XeF_2 would behave similarly. Clearly this is not the case. The weakly absorbed XeF_2 inferred here would not be detected at low pressure, even far below room temperature[8], but would be an important etchant source at higher pressures. In any case the temperature effects, rates and various activation energies strongly suggest that adsorption effects play an important role in the reaction of XeF_2 with silicon, but not with F-atoms.

Chemiluminescence arising from the gas phase reaction of SiF_2 etch product with XeF_2 was observed. The spectrum is identical to those reported in our F-atom[2], SiF_2[12], and F_2[13] studies, but unlike this previous work, the temperature dependence of the luminescent intensity, I_c, does not follow the etch rate in a simple manner. It is important to note that the SiF_2 product yield in XeF_2 is not directly linked to a simple etching mechanism as it is with F-atoms[1] and F_2[13]. Earlier results showed that F-atoms were ≈ 100 times more efficient than F_2 in causing luminescence[1]. Similarity between the energetics of F_2-Si and XeF_2-Si reactions suggests the possibility of a large efficiency difference in favor of F-atoms over XeF_2. Since F-atom contamination of the XeF_2 gas phase is temperature-dependent, we postulate that the complex luminescence may be influenced by small F-atom concentrations. Another contributing factor could be sensitivity of the XeF_2 luminescent reaction to wall and gas temperatures. In any case, the complexity of this temperature-dependent luminescence underscores the previous conclusion that the Si-XeF_2 reaction is fundamentally different from comparable reactions involving F_2 and F-atoms.

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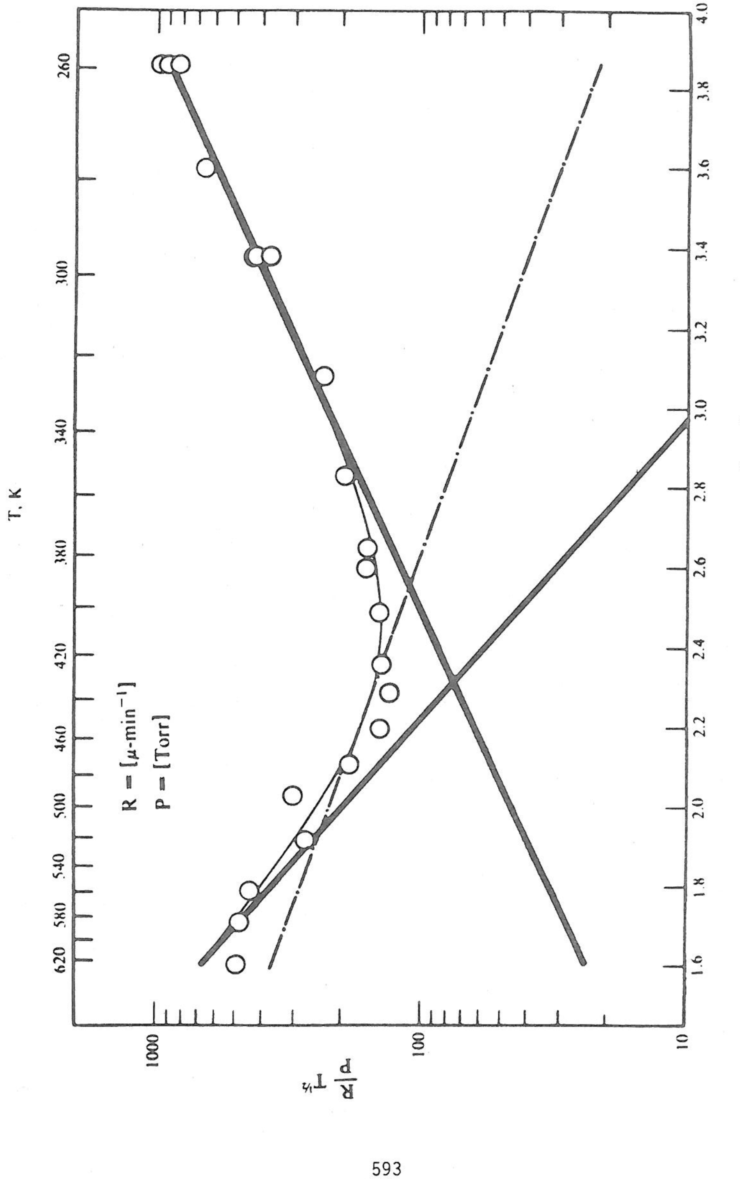
FIGURE CAPTION

Fig. 1. Arrhenius plot of the etch rate of silicon normalized by the flux of XeF_2 (open circles) and F-atoms (dot-dashed line). Data were taken between 0.05 and 0.2 Torr. Asymptotic fits to the XeF_2 data are the bold lines and the smooth curve through the data is the sum of the asymptotic rates.


T, K
260
300
340
380
420
460
500
540
580
620
1/T x 10³, K⁻¹
1.6
1.8
2.0
2.2
2.4
2.6
2.8
3.0
3.2
3.4
3.6
3.8
4.0
R/P T^½
1000
100
10
R = [μ-min⁻¹]
P = [Torr]