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ION-ENHANCED CHEMICAL REACTION OF XeF_2 WITH SILICON BY MODULATED MOLECULAR BEAM MASS SPECTROMETRY

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**Chemistry and Materials Science Division of Lawrence Livermore National Laboratory

ABSTRACT

The reaction of XeF_2 with the Si(100) surface was studied by modulated (10-1000 Hz) molecular beam-mass spectrometry in the temperature range 300-1300K and equivalent XeF_2 pressure of $5x10^{-6}$ to 10^{-4} Torr. Simultaneous bombardment of the reacting surface by Ar^+ was used to determine the extent of ion-enhancement of the reaction.

In the absence of the ion beam, the main reaction product was SiF_4, which was formed with a reaction probability of $\sim 5x10^{-2}$ at room temperature. In the presence of the ion beam three products, SiF_4, SiF_2 and F_2 (or F), were detected with formation probabilities of $\sim 1x10^{-1}$, $6x10^{-2}$ and $7x10^{-2}$ respectively. Increasing surface temperature reduced the ion-enhanced reactivity.

INTRODUCTION

It is well established that the etching rate of some materials with reactive gases can be greatly enhanced by simultaneous exposure to energetic ions[1]. However, the detailed mechanisms by which the ions participate in the gas-surface reactions is not yet understood.

For the silicon-fluorine system, which has been most frequently studied, two different interpretations exist of available experimental results of ion-enhanced reactivity. Donnelly and Flamm[2] believe that energetic ion bombardment causes extensive surface damage on Si. As a result, the impinging molecules react faster on the damage sites, thereby accelerating the etching rate. Coburn and co-workers[3] on the other hand, support the notion that the ions efficiently remove the partially-fluorinated silicon species adsorbed on the silicon and in so doing generate clean surface which reacts rapidly with the incident fluorine.

In the present work, the reaction of XeF_2 with Si(100) was studied by modulated molecular beam-mass spectrometry. The method has been proven to be well-suited for basic studies of gas-surface reaction kinetics because the beam modulation feature provides a direct measure of characteristic response times of the surface processes.

EXPERIMENTAL

A schematic of the apparatus is shown in Fig. 1. It consists of three differentially-pumped vacuum chambers separated by beam-forming orifices. The incident XeF_2 beam is generated by effusion from a quartz source tube which has a hole in the end. A rotating toothed disk modulates the molecular beam at frequencies from 10 to 1000 Hz, which permits reaction times as low as 5μs to be detected. The intensity of the incident molecular beam during the "on" portion of the chopping cycle can be calculated from the gas pressure in the source. The Si target is heated by radiation. It can be bombarded by ion beam for either cleaning or for ion-assisted reaction studies. Portions of the scattered reactant beam and the desorbed reaction products are detected by a quadrupole mass spectrometer mounted in the detection chamber.

The output from the mass spectrometer is processed by a lock-in amplifier to yield the first Fourier components of the signals from scattered reactant (XeF_2) or from reaction products (SiF_4, SiF_2, F_2). The apparent reaction probability ε (the ratio of the product and reactant fluxes) and the phase lag, Φ, which is the difference between the product and the reactant phase angles, are obtained from information provided by the lock-in amplifier. These quantities can also be calculated from theoretical models of the surface processes, and so provide the means of testing potential mechanisms against the data. Each data point is a combination of ε and Φ which is represented as a reaction product vector $\varepsilon e^{i\Phi}$ in the complex plane.

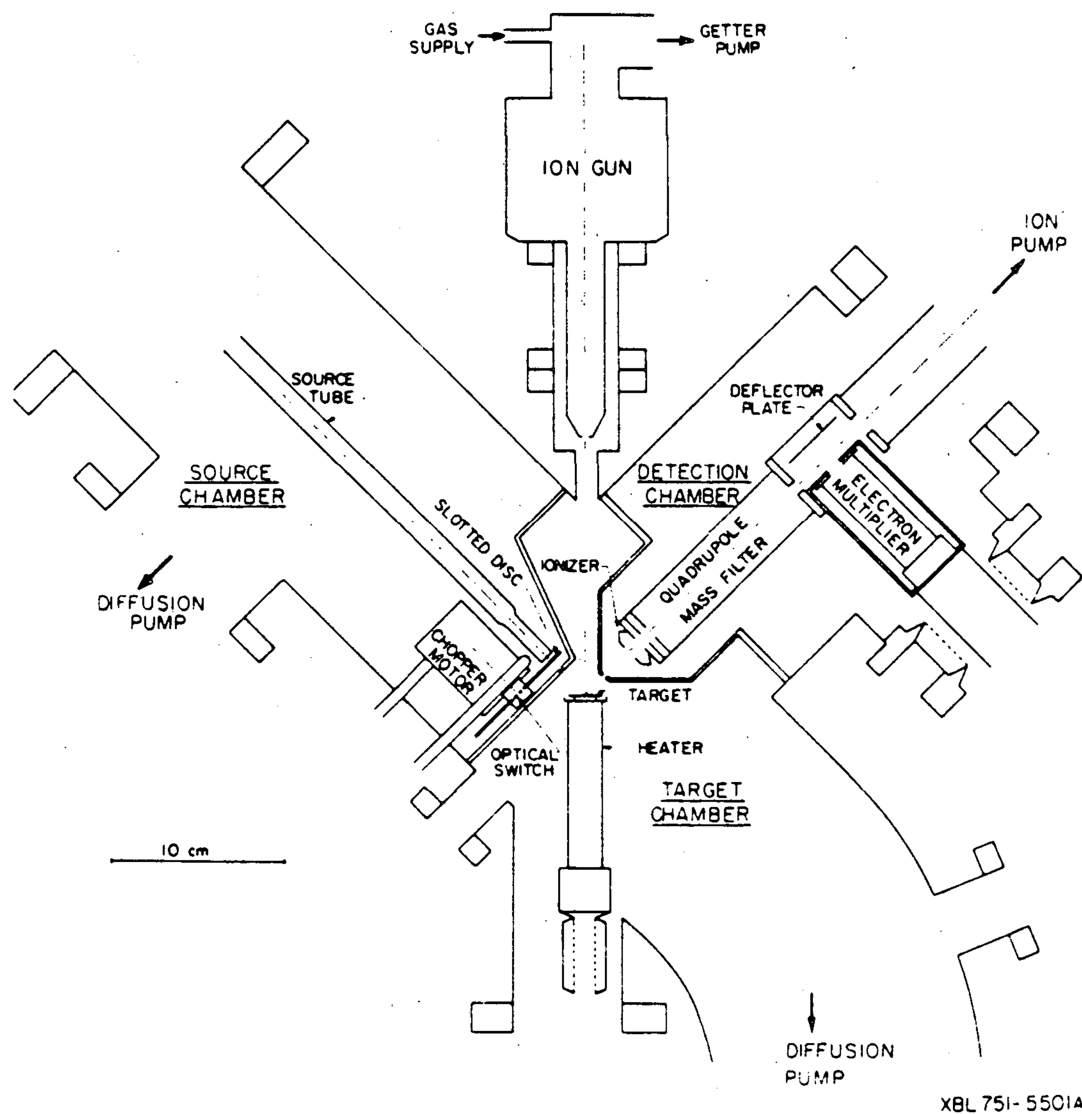

Fig. 1. Modulated Molecular Beam/ modulated ion beam system

RESULTS

It is not trivial to extract the apparent reaction probabilities and phase lags for a complicated system as Si/XeF_2 from mass spectrometer signals. As shown in Fig. 2, the XeF_2 reactant flux, $f^R_{XeF_2}$, results in five products entering to the ionizer of the mass spectrometer. Each output signal from the ionizer is associated with one or more products. The Xe^+ signal, for example, is the combination of simple ionizion of Xe atoms with cracking efficiency of $a^{Xe}_{Xe^+}$ and XeF_2 molecules with cracking efficiency of $a^{XeF_2}_{Xe^+}$. The signal can be therefore related to the product fluxes f^P_{Xe} and $f^P_{XeF_2}$ by the relation:

$$S_{Xe^+} \alpha \frac{f^P_{XeF_2} a^{XeF_2}_{Xe^+} \sigma_{XeF_2} t_{Xe^+} b_{Xe^+}}{v_{XeF_2}} + \frac{f^P_{Xe} a^{Xe}_{Xe^+} \sigma_{Xe} t_{Xe^+} b_{Xe^+}}{v_{Xe}} \quad (1)$$

where σ_i, t_i, b_i and v_i are the ionization cross section, transmissivity of the quadrupole, efficiency of electron multiplier and velocity of molecules at the ionizer, respectively, for species i. These quantities are estimated from the literature. The cracking patterns are deduced from direct line-of-sight measurements of Xe and XeF_2 beams in separate tests.

The reaction product vectors, defined in terms of apparent reaction probabilities and phase lags [4] can be written as,

$$\epsilon_{SiF_4} e^{-i\phi_{SiF_4}} = \frac{2\tilde{f}^P_{SiF_4}}{\tilde{f}^R_{XeF_2}} \quad (2)$$

for the SiF_4 product and

$$\epsilon_{SiF_2} e^{-i\phi_{SiF_2}} = \frac{\tilde{f}^P_{SiF_2}}{\tilde{f}^R_{XeF_2}} \quad (3)$$

for the SiF_2 product.

$\tilde{f}^P$ and $\tilde{f}^R$ are the first Fourier components of the product and reactant fluxes (Fig. 2) which must be determined from the amplitude and phase measurements of the lock-in amplifier signals. The incident reactant flux, $\tilde{f}^R_{XeF_2}$, is obtained in separate tests by measurement of the XeF^+ and Xe^+ signals when an XeF_2 beam is reflected from a nonreacting teflon surface.

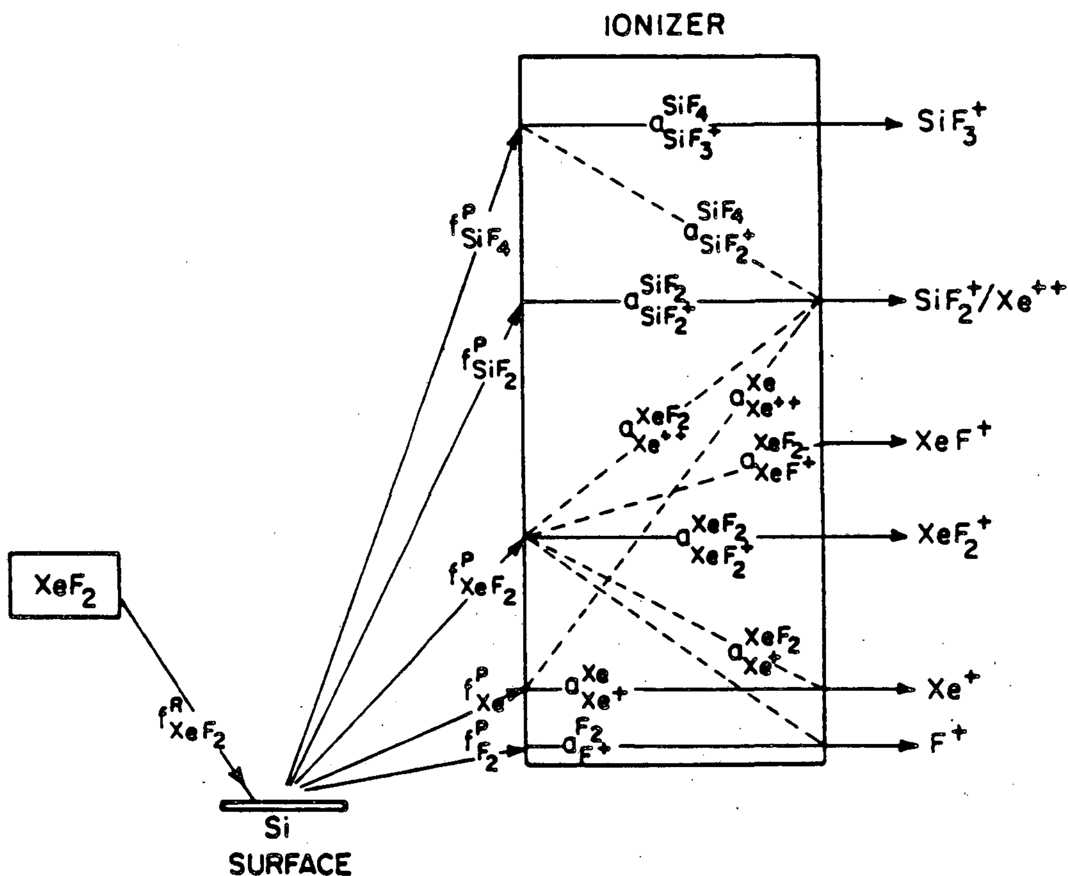

Fig. 2. Cracking patterns of reflected and reaction products due to XeF_2 beam on Si surface in the ionizer of mass spectrometer (electron energy = 70 ev).

The vector $\tilde{f}^P_{SiF_4}$ can be obtained in a straightforward manner from the magnitude and phase of SiF_3^+, after correcting for the amplitude attenuation and phase lag due to SiF_4 transit from the surface to the detector[5]. The magnitude and phase of the combined SiF_2^+/Xe^{++} signals, on the other hand, are consequence of the vectorial sum of the SiF_2, XeF_2 and Xe fluxes weighted by their cracking efficiencies. Measurements of the amplitudes and phases of the Xe^+ and XeF^+ signals, corrected again for transit effects, permits determination of the portion of the signal which arises solely from the SiF_2 flux ($\tilde{F}^P_{SiF_2}$).

Figure 3 shows the apparent reaction probabilities and phase lags for the production of SiF_4 for the thermal gas-surface reaction (labeled as "OFF") and for the reaction assisted by a beam of 3-Kev Ar^+ ions ($\sim 20 \mu A/cm^2$ intensity) covering the total surface area os silicon exposed to the reactant XeF_2 beam (labeled as "ON"). The enhancement due to ion bombardment on the production of SiF_4 is about a factor of 2 for an unheated silicon target and is reduced as the target temperature increases. It was observed that the enhancement at room temperature is strongly time-dependent for fresh samples. Enhancement of as much as a factor of 3 is observed initially, which reduces gradually to a factor of 2 in two hours exposure to a molecular beam of an intensity of $\sim 1 \times 10^{+16}$ molecules/cm^2 s. The phase lags are reduced by ion bombardment at all temperatures. The latter observation indicates acceleration of the surface reaction (i.e., smaller surface residence times) by the energetic ions.

The apparent reaction probabilities and phase lag, for the production of SiF_2 assisted by ion bombardment are shown in Fig. 4 as functions of silicon target temperature. The apparent reaction probabilities for this product increase with temperature and the phase lags decrease with temperature. Comparison with the phase lag of SiF_4 shows that ΦSiF_2 is larger at all temperatures. No SiF_2 product is detectable in the purely thermal reaction.

Some enhancement of the production of F_2 and/or F is also observed with ion bombardment, although no attempt was made to identify the molecular or atomic nature of this product. With ion bombardment, a reaction probability of $\sim 7 \times 10^{-2}$ for the production of F_2 and/or F is estimated.

DISCUSSION

In addition to the reaction product vectors defined by Eqs. (2) and (3) for the volatile silicon products, a reaction probability which measures the emission of elemental xenon from the surface can be written as:

$$\varepsilon_t = f^P_{Xe} / f^R_{XeF_2} \tag{4}$$

This reaction probability, although measured spearately, is related to the SiF_4 and SiF_2 reaction probabilities by material balances on xenon and fluorine.

Referring to Fig. 2, conservation of xenon gives:

$$f^R_{XeF_2} = f^P_{XeF_2} + f^P_{Xe} \tag{5}$$

and conservation of F_2 is expressed by:

$$f^R_{XeF_2} = 2f^P_{SiF_4} + f^P_{SiF_2} + f^P_{XeF_2} + f^P_{F_2} \tag{6}$$

Equating the right hand sides of these balances and dividing by the incident XeF_2 flux gives:

$$\varepsilon_t = \varepsilon_{SiF_4} + \varepsilon_{SiF_2} + \varepsilon_{F_2} \tag{7}$$

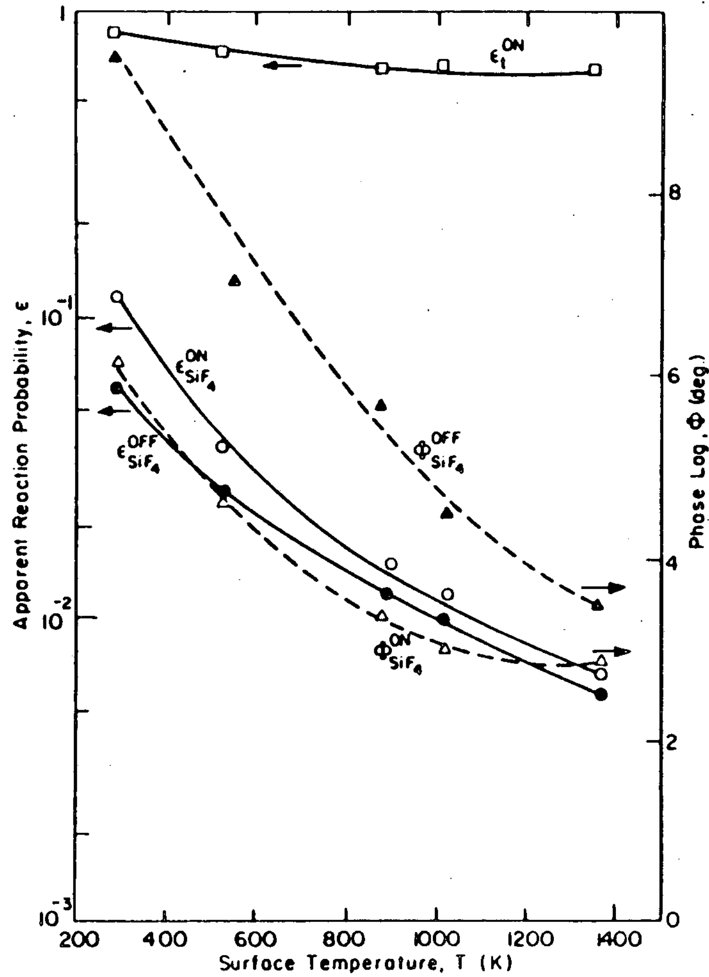

Fig. 3. Production probabilities and phase lags of SiF_4 as a function of Si surface temperature for thermal ("OFF") and ion-assisted reaction ("ON").

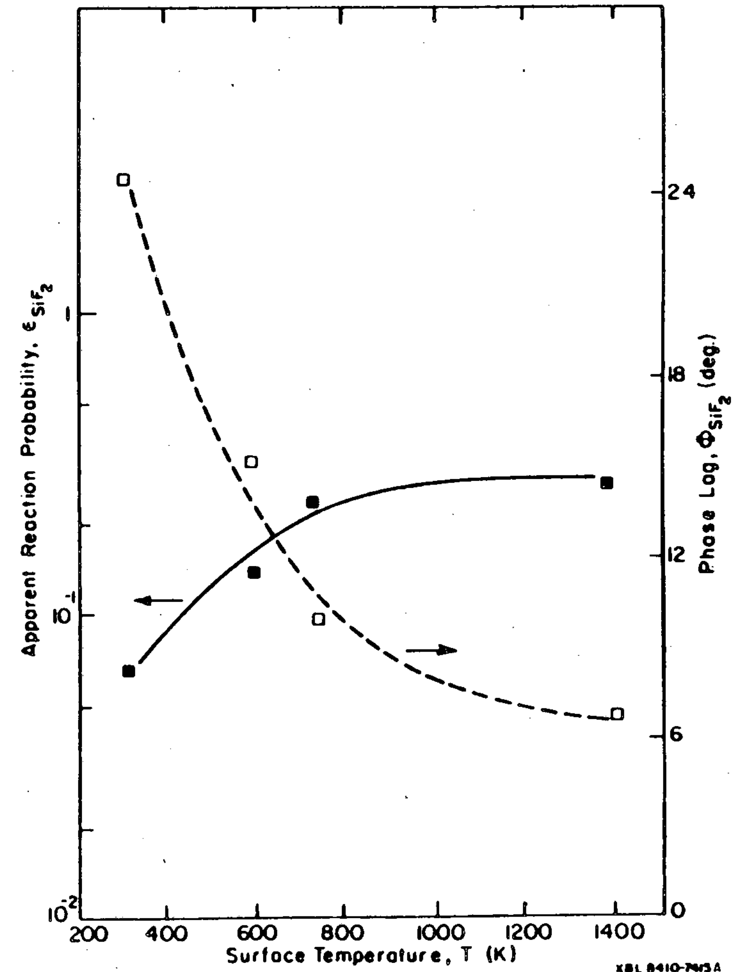

Fig. 4. Production probability and phase lag of SiF_2 as a function of Si surface temperature for ion-assisted reaction.

For the purpose of testing material balance closure, signal attenuation associated with non zero phase lags of the species appearing in Eq.(7) has been neglected. This simplification is acceptable because all measured phase lags are small at low modulation frequencies. Under these conditions the amplitude of the modulated signals are very nearly the same as those that would be measured in a steady state experiment, and so can be used for testing species conservation in the experiments.

At room temperature, ε_t for the ion-assisted reaction is found to be $\sim$0.7. For the same conditions, the sum of the measured reaction probabilities on the right hand side of Eq.(7) is <0.25. Thus some feature of the surface interaction or of the experiment proper is manifest as an apparent failure of Xe and F_2 conservation. Possible causes are discussed below.

The discrepancy could be due to partial dissociation of XeF_2 in the source tube prior to striking the silicon surface. Loudiana and co-workers [6] estimated 50% dissociation of XeF_2 exiting from their doser. Some degree of dissociation is evidence from a line-of-sight phase measurements of pure Xe beam and the molecular beam of vaporized XeF_2 but the degree of dissociation could not be determined because of the lack of cracking patterns of pure XeF_2. There is also some evidence from the frequency dependence of the SiF_3^+ signals that the SiF_4 product desorbs with higher average velocity than expected from thermal emission. This explanation is in accord with the observation of Haring et al.[7] that the energy distribution of the SiF_4 emitted from the Si surface could not be explained by thermal desorption at the target temperature. They interpreted the results by a collision-cascade-like mechanism with a low surface binding energy. If accounted for in the analysis, this effect would increase the magnitudes of the SiF_4 reaction probability by a factor proportional to the ratio of the average desorbed velocity to the thermal value. Finally, there are parameters estimated in the evaluation of reaction probabilities (mainly transmission and electron multiplier efficiencies) which might have had different mass or species dependencies than those assumed.

CONCLUSION

The only detectable reaction product resulting from etching the silicon surface by thermal beams of XeF_2 beam is SiF_4. The reaction probability at room temperature is estimated to be $\sim 6\times10^{-2}$, decreasing with surface temperature. The reaction is slightly higher than first order with respect to the XeF_2 beam intensity.

The maximum enhancement in reactivity over the thermal reactions due to ion bombardment estimated to be about a factor of three. This is in contrast to the earlier results[1] in which enhancement as high as a factor of 20 was observed. The effect is surface-temperature-dependent; it is negligible as the surface temperature approaches the melting point. Beside an enhancement in the production of SiF_4 by almost 100%, a considerable amount of SiF_2 is also observed during ion bombardment while the XeF_2 impinges on the surface. This product, unlike SiF_4, increases with temperature.

The phase lags, which are measures of surface residence times for formation of a product, are generally smaller when the reaction is assisted by the ion beam. This would not be the case if the sole effect of the energetic ions were the creation of damage sites, which would alter only the magnitude of the reaction probability. The phase lag reduction can be explained by the acceleration of one or more intermediate steps of the surface reaction.

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