Deuterium and fluorine radical reaction kinetics on photoresist*

Frank Greer, J. W. Coburn, and David B. Graves a)
Department of Chemical Engineering, University of California, Berkeley, California 94720

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The etching of two photoresists (PR) was investigated using beams of Ar$^+$ ions and neutral fluorine and deuterium atoms. Large increases in the PR etch yields were observed as the flux ratio of the fluorine atom to the Ar$^+$ ion beam was increased. However, there was no observed effect of deuterium on the PR etch yield despite the detectable formation of DF during the etching process. To explain this observation, the following abstraction and recombination probabilities from the PR surface were measured using modulated beam mass spectrometry: F atoms abstracting adsorbed D atoms ($\gamma_{DF}=0.19$), D atoms abstracting adsorbed F atoms ($\gamma_{DF}<0.05$), and D atoms recombining with adsorbed D atoms ($\gamma_{DD}=0.06$). These measurements were insufficient by themselves to make any conclusive statements about the observed independence of the etch yield on D atom flux, so a phenomenological model of the PR etching process was developed to explain the observed phenomena. When these measured quantities were used as parameters in this model, it was possible to predict the observed lack of effect of D atoms on the PR etch yield. During the course of these experiments, the etching probability of a D atom was also measured ($1.5\times10^{-4}$) and found to be in good agreement with previously published values.

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I. INTRODUCTION

It has long been accepted that atomic fluorine plays a key role in determining the etch rates of many different materials in an industrial plasma reactor. However, there is still little known about many of the reactions that govern the F atom concentration in these reactors. This is especially true for the case of high-density fluorocarbon oxide etch plasmas. In these plasmas, fluorine atoms are believed to play an important role in determining the etch rate selectivity for silicon dioxide over silicon, silicon nitride, and photoresist. For example, it has been shown that the introduction of hydrogen in the inlet gas stream improves these selectivities, presumably by reducing the concentration of F atoms in the tool. Hydrogen atoms are thought to combine with fluorine at surfaces and in the gas phase to produce HF, but little quantitative information is available to help predict the rates of these reactions.

In order to model plasma reactors and accurately predict etch rates of materials of interest, it is important to develop a fundamental understanding of radical reactions at surfaces and how they alter the fluorine radical balance in the tool. These reactions are difficult to study in most plasma reactors due to the coupling of the gas phase and surface chemistry and the overwhelming number of variables affecting the plasma and surface conditions. These problems can both be addressed by performing experiments in a vacuum beam system. In a beam system, surfaces of interest are exposed under well-controlled, high vacuum conditions ($\sim 10^{-6}$ Torr) to beams of active species, such as F atoms and H atoms, that are representative of those found in a plasma reactor. Since the beams are well-characterized, it is possible to obtain reliable measurements of the reaction probabilities of the species of interest as a function of the surface type, surface temperature, and other variables of interest.

In a previously published work, the etching of two types of photoresist (PR) was investigated using beams of Ar$^+$ ions and neutral fluorine and deuterium atoms. Large increases in the PR etch yields were observed as the flux ratio of the fluorine atom to the Ar$^+$ ion beam was increased. However, there was no observed effect on the PR etch yield when the PR was simultaneously exposed to F atoms, Ar$^+$ ions, and deuterium atoms despite the detectable formation of DF during the etching process. In this work, the observed lack of D atom effect is investigated by measuring various rates of reactive species abstraction from the PR surface using modulated beam mass spectrometry. The values of the parameters measured in these experiments were then used in a phenomenological model to explain the observed phenomena. This model predicts the fluorine and deuterium coverage on the PR surface as a function of all of the incident fluxes.

Since the PR etch yield is assumed to be linearly dependent on the fluorine coverage the model also predicts the PR etch yield.

II. EXPERIMENT

A. Main chamber and samples

The experimental apparatus, which has been described in detail previously, consists of a differentially pumped, high vacuum chamber containing a rotatable carousel on which several samples are mounted (see Fig. 1). Shipley System 805 (g-line) and Olin 101 (i-line), two positive tone photoresists typical of those used in silicon dioxide etching, were used in this series of experiments. The photoresists were deposited via spin coating on QCM substrates to a thickness of approximately 1 $\mu$m and subsequently baked at 120 $^\circ$C for...

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*a) No proof corrections received from author prior to publication.

b) Electronic mail: graves@uclink4.berkeley.edu
20 min. By depositing the photoresist on QCM substrates, it is possible to make in situ, real time measurements of the PR etch rate and of the adsorption of fluorine and deuterium atoms on the PR surface.

The base pressure in the main chamber is $10^{-7}$ Torr and the pressure during the source operation is in the low $10^{-6}$ Torr range. The high vacuum conditions were required to ensure that the mean free path of a gas molecule in the chamber is greater than the dimensions of the chamber. Thus, species evolved or reflected from the sample surface can be detected, without suffering a gas phase collision, by a quadrupole mass spectrometer (QMS). The QMS is mounted in the analysis section of the apparatus, and is positioned so that it lies along the line of sight with the sample surface. The analysis section is separated by four stages of differential pumping from the main chamber, allowing the base pressure in the mass spectrometer chamber to reach the $10^{-10}$ Torr range. To distinguish between the species originating at the surface and those coming from background gas, modulated beam mass spectrometry was used.

B. Argon ion, deuterium atom, and fluorine atom sources

The beams of atomic deuterium and atomic fluorine were created with two independently controlled external plasma sources mounted on the chamber. Both sources have been described in detail previously. The degrees of dissociation of the sources were estimated to be approximately 25% for D and 30% for F in these experiments. This means, for example, that the beam from the D atom source was 40% D atoms and 60% $D_2$ molecules. The fluorine atom flux was varied from 0 to $6 \times 10^{15}$ atoms/cm$^2$/s by adjusting the inlet pressure of fluorine gas to the source while the deuterium atom flux was varied from 0 to $2 \times 10^{16}$ atoms/cm$^2$/s by a similar procedure.

Deuterium is used in these experiments for two reasons. Background hydrogen in the QMS makes the detection of H and $H_2$ difficult, reducing the accuracy of the calculation of the percentage dissociation of the flux. Detection of HF$^+$ (mass to charge ratio=20) is also complicated by the presence of a peak in the QMS resulting from doubly ionized argon, Ar$^{2+}$ (also mass to charge ratio=20). This signal cannot be eliminated due to the use of argon in the ion gun and in the D and F atom sources to assist in their ignition. DF$^+$ (mass to charge ratio=21) is not obscured by other species in the QMS, and therefore, DF generated at the PR surface can be detected.

The argon ion flux was obtained from a commercial ion gun (Phi Electronics). The ion energy, either 500 or 1000 eV, was selected on the ion gun controller. By adjusting the pressure in the ion gun chamber, a flux of Ar$^+$ ions ranging from $5 \times 10^{12}$ to $5 \times 10^{13}$ ions/cm$^2$/s was used. Etch rate experiments with fluorine atom/argon ion flux ratios varying from 0 to 800 were made by adjusting both the ion flux and the atom flux. To neutralize the insulating PR sample surface during ion bombardment, an electron flux was obtained from a tungsten filament.

C. Experimental procedure

All etching and abstraction experiments were performed at 13 °C ± 2 °C. During these experiments, the sample studied was positioned in the center of the main chamber at the intersection of the atom and ion beams. The ion gun and the deuterium atom source are mounted in a plane that makes an angle of 27° to the sample surface normal while the fluorine atom source makes an angle of 45°. A Faraday cup, also mounted on the carousel, was used to measure the ion current from the ion gun.

The etching experiments and their results are described in detail elsewhere. The abstraction experiments were conducted in the following manner. To begin, a PR sample was chosen and then exposed to a beam of fluorine atoms. These atoms were observed to chemisorb on the PR and the mass change of the sample was monitored during the fluorine atom exposure. This exposure was made for 1 h to ensure saturation. Once the PR was fluorinated in this manner, the sample was exposed to a beam of deuterium atoms. The purpose of
this exposure was to measure the rate of formation of DF due to D atoms abstracting F from the PR.

Two quantities were monitored during the exposure of the samples to D atoms. First, a QMS was used to detect DF evolved from the surface of interest. Second, the PR coated QCMs were monitored to detect changes in their mass. The samples were also exposed to the D atom beam for 1 h. After the D atom beam exposure, the deuterated samples were then exposed again to a beam of F atoms. During this fluorine atom exposure, the DF formed on the surface due to F atoms abstracting D from the surface was again monitored using the QMS. The PR QCM was monitored during this exposure to determine the mass change of the sample caused by the F atom beam.

These two processes, D exposure followed by F exposure, were repeated for several cycles. This caused each sample to cycle between a deuterated and a fluorinated surface, respectively. In this way, the abstraction probability of F atoms for adsorbed D atoms and the converse was measured repeatedly under the same conditions to obtain reasonable statistics for the reaction rate coefficients.

**III. RESULTS**

**A. Qualitative features of D and F abstraction results**

To explain the lack of D atom effect on the PR etch yield, it was necessary to measure the relative reactivities of F and D atoms toward self-abstraction and cross-abstraction from the PR surface. Figures 2(a) and 3 show results typical of those observed in the QMS during the F and D exposures of the PR sample. The data in Fig. 2(a) show that when PR is first exposed to D atoms and then is exposed to F atoms, DF is initially formed on the surface very rapidly. The rate of DF formation slows as the surface is depleted of D atoms until essentially all of the D atoms have been removed and have been replaced by fluorine atoms. However, when this fluorinated PR is then exposed to D atoms, DF is not observed as a reaction product (see Fig. 3). Thus, the QMS data indicates that F atoms will readily abstract D from the PR surface, while it appears that D atoms will not abstract F atoms at a detectable rate.

This result is perhaps not surprising given the data avail-
able for the analogous gas phase reactions. These gas phase reactions are as follows: (1) a gas phase fluorine atom abstracts an H atom from methane to form HF and a methyl radical, and (2) a gas phase hydrogen atom abstracts an F atom from CF₄ to form HF and a CF₃ radical. Since the abstraction process on the PR surface involves either the breaking of a C–F bond or a C–H bond by reaction with a radical, it is reasonable to compare these two sets of reactions:

\[ \text{CH}_4(g) + F^*_g \rightarrow \text{CH}_3^* + \text{HF}(g), \]  

(1)

\[ \text{CF}_4(g) + H^*_g \rightarrow \text{CF}_3^* + \text{HF}(g). \]  

(2)

The activation energy of reaction (1) is \( \sim 10^5 \) times less than that of reaction (2).² This, thus, there is a much larger energetic barrier for a hydrogen atom to overcome in order to abstract fluorine from a carbon atom than for the converse. This difference in activation energy is most likely related to the relative bond strengths of the C–F and C–H bonds. The C–F bond strength is about 4.7 eV while the C–H bond strength is 3.5 eV.⁶ It is likely that the C–F and C–H bonds formed on the PR surface will have similar relative bond strengths and reactivities to those reported for gas phase species. Thus, the result that D atoms cannot abstract F atoms from PR at any detectable rate under these conditions while the converse reaction proceeds quite readily is not surprising.

The significance of this result is that \( \gamma_{FD} \) is non-zero, while \( \gamma_{DF} \) is nearly zero (note: these parameters, and others used throughout the rest of the article, are listed in Table III). In the following section, \( \gamma_{FD} \) will be quantitatively determined, and in further sections, it will be shown that this result ensures that D atoms have no measurable effect on PR etch yield in these experiments.

### B. Abstraction probability of F atoms

The absolute abstraction probability of D atoms by F atoms can be determined quantitatively from the QMS data. The rate of D abstraction from the chosen surface can be represented by the following simple rate expression:

\[ \sigma^* \frac{d\theta_D}{dt} = -\gamma_{FD} \Gamma_F \theta_D, \]  

(3)

where \( \sigma^* \) = reactive site density (atoms/cm²), \( \gamma_{FD} \) = F abstraction probability for adsorbed D, \( \Gamma_F \) = incident fluorine atom flux (atoms/cm²s), and \( \theta_D \) = D atom coverage on the surface. This equation can be rearranged to solve for the change in D atom coverage as a function of time. This yields the following expression that is an exponential decay in the D atom coverage:

\[ \theta_D = \theta_{D,0} \exp \left(-\gamma_{FD} \Gamma_F \sigma^* \right), \]  

(4)

where \( \theta_{D,0} \) = the initial coverage of D atoms. This model can be fit to the QMS data to obtain the abstraction probability [see Fig. 2(b)]. The initial characteristic decay time of the process (\( \tau = \sigma^*/\gamma_{FD} \Gamma_F \)) was found to be 50 (±5) s for PR. Before \( \gamma_{FD} \) can be determined, however, an estimate must be made for the reactive site density, \( \sigma^* \). This can be made from the total mass gain of the PR after F atom exposure using the following formula:

\[ \sigma^*(\text{atoms/cm}^2) = \frac{\text{Total Mass Gain (amu)}}{17 \text{(Net amu Gain/Atom)} \times \text{Area (cm}^2\text{)}}. \]  

(5)

The term 17 amu/(atom exchanged) comes from replacing a D atom (2 amu) with an F atom (19 amu). \( \sigma^* \) was determined to be 1.5 (±0.4) × 10⁷ amu/cm² from mass uptake measurements made by the QCM. With this value for \( \sigma^* \), the abstraction probability, \( \gamma_{FD} \), was determined to be 0.19 (±0.04).

However, as is evident from a comparison of Figs. 2(a) and 2(b), the model does not capture the abstraction process completely for longer times. One possible explanation for this observation is that not all of the active sites are equally accessible to the incident fluorine atom flux. If only a certain fraction of the PR active sites lie on the very top surface, fluorine atoms from the incident beam must diffuse into the mixed layer at the PR surface before reacting with more deeply buried D atoms. The DF product must then diffuse back to the surface before desorbing. This would account for the reaction rate apparently slowing over time as the most easily accessible D atoms are removed first, leaving atoms that are more difficult to abstract due to the diffusion limitations of the reactant F and product DF.

### C. Recombination probability

In addition to the abstraction probability, it is also important to know the recombination probability of each radical on the PR surface. The process of radical recombination on surfaces does not result from the interaction of two physisorbed atoms diffusing on the surface.⁴ Recombination has been shown to be the result of a gas phase atom abstracting an atom of the same type that has previously chemisorbed to the surface. Since recombination lowers the number of atoms that are bound to the surface, the reactive species coverage is clearly reduced by this process. While previous measurements have shown that the F atom recombination rate on PR is below the detection limits of this apparatus,⁴ it has been shown that H atoms will recombine on Si quite readily to form H₂.⁷ Therefore, it was reasonable to assume that this process might be very important on PR.

The procedure used to measure the recombination coefficient for D on PR is described in the Appendix, and has also been described previously in detail.⁴ It relies on the assumption that the recombination of many different atomic species is below the detectable limits of this apparatus on room temperature quartz surfaces. The measured D atom recombination probability was approximately 0.06 (±0.05), just above this method’s detection limit of ~0.05. While this value on PR is smaller than on Si, it still shows that recombination is a significant mechanism for lowering the deuterium coverage on the PR surface.
D. Phenomenological modeling

Despite the quantitative information given by the various reaction probabilities measured and discussed above, some model of the etching process is required to make conclusive statements about the why the PR etch yield is independent of the D atom flux when F atoms are present. To develop this model, we start with a discussion of the mixed layer that forms during ion enhanced etching of materials. Many different processes take place in this layer, including adsorption and diffusion of reactants; formation, diffusion, and desorption of reaction products; radical abstraction reactions; etc. To accurately model the etching process at a surface, one must account for all of these processes that take place in this mixed layer. One way to do this is to draw a control volume that encompasses the entire mixed layer as illustrated schematically in Fig. 4. For simplicity of mathematical analysis, the total amount of PR in the control volume is held constant during the etching process, and the other atomic constituents of PR (oxygen, etc.) are neglected in this analysis. This is done by replacing the material that is etched and removed through the top of the control volume with new, virgin material added through the bottom of the control volume. Thus, the boundaries of the control volume advance at the same rate that the material is etched.

During the PR etching process, fluorine and deuterium are added to the mixed layer due to the adsorption of these reactive species on open active sites on the PR surface. Since in our representation, the amount of PR material (essentially, the number of carbon atoms) in the control volume is held fixed, the total number of active sites in the mixed layer is constant. Therefore, we can define two terms, the fluorine coverage and the deuterium coverage, which are simply ratios of the number of adsorbed atoms (fluorine or deuterium, respectively) to the total number of active sites in the mixed layer of the PR. The coverage of these reactive species in the mixed layer has been shown experimentally to determine the chemical sputtering rate of many different materials. Therefore, many authors have developed phenomenological models of the etching process which describe the etch rate of these materials as linearly dependent on reactive species coverages. In order to predict these coverages, these models contain mathematical expressions that quantify the important physical processes taking place in the mixed layer.

To use this method to develop a predictive model of the PR etching process in our beam experiments, we chose to consider the following types of physical processes: ion enhanced chemical sputtering of PR, physical sputtering of PR, chemisorption of both fluorine and deuterium radicals on open active sites, and radical abstraction of species from the PR surface (see Fig. 4). Since each of these processes impacts the coverage of fluorine and deuterium in different ways, two coupled differential equations for the rates of change of these coverages can be written where each term corresponds to one of these physical processes. At steady state, the time derivatives are equal to zero, and the form that these equations take is as follows:

\[
\frac{d(\theta_D \theta_F^*)}{dt} = s_F \Gamma_F (1 - \theta_F - \theta_D) - J_{Ar^+} Y_{Ch} \theta_F = 0,
\]

\[
\frac{d(\theta_D \theta_F^*)}{dt} = s_D \Gamma_D (1 - \theta_D - \theta_F) - J_{Ar^+} Y_{Ch} \theta_F \theta_D
\]

The parameters in the rate expressions are defined in Tables I, II, and III.

The final term in the expression for the deuterium coverage does not correspond to any specific physical process, but is in fact a consequence of our choice of control volume.

### Table I. Controlled variables.

<table>
<thead>
<tr>
<th>Variable description</th>
<th>Symbol</th>
<th>Typical variable value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fluorine atom flux to PR surface</td>
<td>$\Gamma_F$</td>
<td>$-10^{15} \text{ cm}^{-2} \text{ s}^{-1}$</td>
</tr>
<tr>
<td>Deuterium atom flux to PR surface</td>
<td>$\Gamma_D$</td>
<td>$-10^{15} \text{ cm}^{-2} \text{ s}^{-1}$</td>
</tr>
<tr>
<td>Argon ion flux to PR surface</td>
<td>$J_{Ar^+}$</td>
<td>$-10^{13} \text{ cm}^{-2} \text{ s}^{-1}$</td>
</tr>
</tbody>
</table>
Since virgin PR is added to the control volume from the bottom to replace the PR that is etched during ion bombardment, hydrogen atoms are therefore carried into the control volume bound to the carbon atoms that make up the PR. The model essentially treats this as an additional input of hydrogen atoms into the mixed layer. For simplicity, the reactivities of hydrogen and deuterium atoms are assumed to be the same.

The introduction of these mathematical expressions introduces several parameters that describe the probability of each of these processes. To obtain quantitative information from the model about the PR etching process, it is necessary to determine values for these parameters either experimentally, or through reasonable assumptions. Two of these parameters, $\gamma_{FD}$ and $\gamma_{DD}$, were measured directly and have been discussed previously in this paper. They can be directly incorporated into the model.

Two of these parameters, $y$ and $z$, cannot be easily measured experimentally. However, there are ways of obtaining reasonable estimates of these parameters. Since $z$ is the number of hydrogen atoms per carbon atom in the PR, it is not difficult to put an upper bound on this number. Since the PR is a polymer, $z$ can be no more than 2 since carbon has a tetravalent structure and the number of bonds formed to other carbon atoms must be at least two to form a chain. $y$ is closely related to $z$ since $y$ represents the maximum number of hydrogen atoms that can leave with a sputtered carbon atom. Our previous results have suggested that the PR may be sputtered as small fragments of polymer chains. Therefore, $y$ is likely around 2 for the same reasons that $z$ is bounded by that value. Since these two parameters multiply terms with opposite signs, inaccuracies associated with these assumptions tend to cancel.

An additional three parameters, $x_F$, $x$, and $Y_{Chem}$, are already available based on our previous experiments with Ar$^+$ and F atom beams without D atoms. Unfortunately, these parameters were derived without considering hydrogen abstraction from the PR surface by the incident fluorine atom flux. However, it is fairly straightforward to adjust these coefficients to take this into account. The phenomenological model presented in this paper can simply be applied for the case where the incident D atom flux is zero. This eliminates several terms from the D coverage expression, allowing the model to be fit to determine $Y_{Chem}$. The rest of the parameters are self-consistently determined using the previously collected QMS and QCM data in the method described in a previous article. With these assumptions and measurements, nearly all of the parameters in the phenomenological model can be determined. The model as a whole can be considered as a single parameter fit to the data when the incident D flux is equal to zero, since $Y_{Chem}$ is the only parameter in the model.

### Table II. Calculated variables.

<table>
<thead>
<tr>
<th>Variable description</th>
<th>Symbol</th>
<th>Variable range</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fractional fluorine coverage on PR</td>
<td>$\theta_F$</td>
<td>0–1</td>
</tr>
<tr>
<td>Fractional deuterium coverage on PR</td>
<td>$\theta_D$</td>
<td>0–1</td>
</tr>
<tr>
<td>D sticking coeff.</td>
<td>$\gamma_D$</td>
<td>0–0.12</td>
</tr>
</tbody>
</table>

### Table III. Measured/estimated parameter values.

<table>
<thead>
<tr>
<th>Parameter description</th>
<th>Symbol</th>
<th>Measured/estimated parameter value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fluorine sticking coeff.</td>
<td>$s_F$</td>
<td>0.15</td>
</tr>
<tr>
<td>F atom abstraction coeff. of D from PR</td>
<td>$\gamma_{FD}$</td>
<td>0.19</td>
</tr>
<tr>
<td>D atom abstraction coeff. of F from PR</td>
<td>$\gamma_{DF}$</td>
<td>&lt;0.05</td>
</tr>
<tr>
<td>F atom recombination coeff. on PR</td>
<td>$\gamma_{FF}$</td>
<td>&lt;0.05$^b$</td>
</tr>
<tr>
<td>D atom recombination coeff. of PR</td>
<td>$\gamma_{DD}$</td>
<td>0.06</td>
</tr>
<tr>
<td>No. of F atoms bound to each chemically sputtered C atom</td>
<td>$x$</td>
<td>1</td>
</tr>
<tr>
<td>No. of D atoms bound to each chemically sputtered C atom</td>
<td>$y$</td>
<td>2</td>
</tr>
<tr>
<td>No. of H atoms bound to each C atom in virgin PR</td>
<td>$z$</td>
<td>2</td>
</tr>
<tr>
<td>Physical sputtering yield of PR with Ar$^+$ ions</td>
<td>$Y_{Ph}$</td>
<td>3$^a$</td>
</tr>
<tr>
<td>Chemical sputtering yield of PR with Ar$^+$ ions and F atoms</td>
<td>$Y_{Chem}$</td>
<td>60</td>
</tr>
</tbody>
</table>

$^a$Parameter obtained from Ref. 3.
$^b$Parameter obtained from Ref. 4.
which is adjusted to fit the data, while all others are either directly measured or estimated given the likely structure of the PR.

However, when the incident D flux is nonzero, one final parameter, $s_{D}$, must be accounted for. It cannot be easily estimated, but one can determine upper and lower bounds for $s_{D}$ based on fitting the phenomenological model to the PR etching experiments. If the range of values for $s_{D}$ which result in model fits are with a range of physically reasonable values for a sticking probability, then it is reasonable to assume that the phenomenological model is capturing the essential physics of the etching process. The values of all model parameters are listed in Table III.

Figure 5 shows the PR etch yield predicted by the model as a function of $s_{D}$. As our assumed value of $s_{D}$ increases, the predicted EY decreases as more and more of the open active sites are filled with D atoms. Essentially, these D atoms block the adsorption of fluorine atoms from the gas phase, lowering the F coverage. Since the EY is strongly dependent on the F coverage, it decreases as the D coverage increases. Two competing processes slow the rate that the D coverage increases, however. F atom abstraction of and D atom recombination with chemisorbed D on the PR both tend to reduce D coverage. However, after increasing $s_{D}$ to a certain point, the amount that the phenomenological model underpredicts the measured etch yield exceeds 2 C atoms/ion, the approximate scatter in the measured data. This occurs at a deuterium atom sticking probability of around 0.12. Therefore, the phenomenological model should be valid as long as the sticking probability of deuterium on PR falls within a range of 0–0.12. This is certainly very probable since the experimentally determined value of many radical sticking probabilities falls within this range. Unfortunately, without an exact measurement of this sticking probability, it is impossible to be completely certain about the agreement of the model. However, the fact that the model does agree over a fairly wide range of assumed $s_{D}$ values does lend some credence to the model and the interpretations that arise from it.

The most striking feature of the model results is that the independence of the PR EY from the incident D atom flux arises from the large asymmetry in the heteronuclear abstraction probabilities for F and D atoms. It is clearly important that D does not abstract F from PR (γ_{DF} ~ 0) since this process would directly reduce the F coverage, and therefore the PR EY. However, based on the model results, it is also very important that F abstraction of D is large. Without F abstraction of D, D atoms would saturate the open active sites of the PR surface. This would inhibit the adsorption of F, lowering the F coverage and thus the PR EY. Therefore, both processes are clearly important in ensuring the independence of the PR EY on the D atom flux.

E. QCM measurements

During the abstraction experiments, measurements were made of the change in the mass of the PR using the QCM. The abstraction process leads to a mass change because fluorine and deuterium atoms have significantly different masses. When an F atom abstracts a D atom, an open site is left behind. This site is eventually filled by an F atom from the incoming beam. This sequence of events causes the PR to gain 17 amu per active site (the difference in mass between an F atom and a D atom). This process has been observed and will be presented elsewhere. However, since the QMS results show that D atoms do not abstract F atoms, one would expect the mass of the PR sample to remain constant during the D atom exposure.

Figure 6 shows the QCM results from the D atom exposure of the fluorinated PR surface. It is clear that the mass of the PR is changing. Since the mass change cannot be due to the abstraction of F atoms by D from the PR, the mass removal is likely due to the etching of the PR by the D atom beam. Hydrogen atoms have been previously shown to etch organic films. The probability of the D atoms from the incident beam etching a carbon atom from the PR was found to be $1.5 \times 10^{-4}$. This is within a factor of 3 of the previously measured organic film etch rate.

One interesting feature of the data is that the rate of mass
removal seems to be higher initially, after which it slows to a
constant rate. This is not surprising, however, as one must
remember that the top layer of PR is fluorinated. When the D
atom beam is etching this fluorinated layer, the etch products
are more massive since they are partially fluorinated (i.e.,
CF$_x$D$_y$). However, once that top layer is removed, the etch
products are no longer fluorinated, and are therefore less
massive (i.e., CH$_x$D$_y$). Therefore, even though the mass re-
moval rate is changing, the carbon etch rate may be constant.

IV. CONCLUSIONS

A series of experiments have been performed to investi-
gate the reaction kinetics between D and F radicals on a PR
surface in the absence of ion bombardment. It was deter-
mined that the probability for a fluorine atom abstracting a
deuterium atom is 0.19 (±0.05) while deuterium atoms are
incapable of abstracting fluorine atoms from the PR at any
detectable rate. These two results suggest that D abstraction
of F, as compared to F abstraction of D, has a relatively high
activation energy. These two observations are consistent with
available gas phase data for reactions of this type. The re-
combination probability of D atoms on PR was also mea-
sured and was found to be 0.06 (±0.05).

The results of these abstraction and recombination experi-
ments were incorporated into a phenomenological model of
PR etching. The purpose of this model was to quantitatively
predict the results of etching with Ar$^+$ ions, F atoms, and D
atoms, or more specifically the lack of an impact of D atoms
on the PR etch rate. All parameters in the model except for
$s_D$, the sticking probability of D atoms on a bare site, were
either estimated or experimentally determined. By compar-
ing the model fit to the data, it was clear that the possible
range of values for $s_D$ consistent with the etching rate experi-
ments was from 0–0.12, which is reasonable given the val-
ues of radical sticking probabilities that have been previously
reported in other etching experiments. This suggests two
main conclusions. First, the phenomenological model fairly
accurately represents the physical and chemical processes
taking place in the mixed layer of the ion bombarded PR.
Second, for this system, fluorine atom abstraction of hydro-
gen from the PR surface plays a very important role in de-
termining the PR etch rate since this is the key mechanism
by which excess hydrogen that is added to the PR surface
from the gas phase is removed.

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APPENDIX: DETERMINATION OF RECOMBINATION
PROBABILITIES USING MODULATED BEAM
MASS SPECTROMETRY

The following figures and calculations illustrate the
method of determining the recombination probability of D
atoms on PR. When the recombination probability is to be
calculated, there are four sets of data that must be collected
using the QMS. The first two are the signals for D$_2$ reflected
from both the quartz and PR samples with the plasma off
(see part 1 of Fig. 7). These signals will here after be referred
to as $z_{SiO_2}$ and $z_{PR}$. Once these have been measured, the
plasma source is ignited, and two additional sets of data are
collected, the signals for D$_2$ reflected from both the quartz
and PR samples (see part 2 of Fig. 7). The D$_2$ signals, $b_{SiO_2}$
and $b_{PR}$, are lower than the corresponding $z$ values due to
the dissociation of D$_2$ in to D in the plasma source.

The first step is to calculate the degree of dissociation that
has been achieved in the source. This is done by making two
assumptions. First, it is assumed that there is no recombi-
nation of the D atoms on the quartz surface (i.e., $a_{SiO_2} = x_{SiO_2}$
and $b_{SiO_2} = y_{SiO_2}$). As stated earlier, this is not a bad assump-
tion for surface treated quartz. The second assumption is
that the decrease in D$_2$ signal is solely due to the dissociation
of D$_2$ into D atoms, and is not the result of any other loss
process. Since during source operation, there is only deute-
rum and argon in the source, there should be no other means
of consumption of D$_2$. Given these assumptions, the degree
of dissociation $d$ is

$$d = \frac{z_{SiO_2} - y_{SiO_2}}{z_{SiO_2}} = \frac{\text{reflected } D_2}{\text{Original } D_2 \text{ (plasma off)}}.$$  (A1)
Once $d$ has been determined, the recombination probability of D atoms on the PR surface can be calculated. First, we calculate the fraction, $f$, of the original, plasma off, $D_2$ signal that is measured coming from the PR surface with the plasma on:

$$f = \frac{z_{\text{PR}} - b_{\text{PR}}}{z_{\text{PR}}}$$

The difference between these two ratios is due to the recombination of D atoms on the PR surface. The first term in the expression for $f$ is simply $d$. The second term in $f$ can be expressed using the recombination probability $\gamma_{DD}$ and $d$. After some simplification, the expression for $f$ reduces to

$$f = d + \gamma_{DD} d.$$  \hfill (A3)

Therefore, the recombination probability is given by

$$\gamma_{DD} = \frac{f}{d} - 1.$$  \hfill (A4)