Vacuum beam studies of photoresist etching kinetics

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One factor limiting the development of reliable models of high density, low pressure oxide etch plasmas is the relatively poor understanding of the plasma-photoresist surface interactions. In particular, the relatively high rates of photoresist (PR) loss experienced in high density fluorocarbon plasmas is a significant problem. It has long been accepted that fluorine plays a key role in controlling the oxide to PR etch rate selectivity. The addition of hydrogen has been shown to improve this selectivity, presumably by scavenging fluorine from the tool by forming HF. By reducing the fluorine to carbon ratio in the plasma and more specifically at the PR surface itself, the rate of polymer deposition increases causing the net PR etch rate to decrease. In this work, the complex surface chemistry of fluorocarbon plasmas is simplified to facilitate the study of the interaction of fluorine atoms and hydrogen atoms on the PR surface. This chemistry is modeled in vacuum beam experiments with argon ions and independent fluxes of neutral deuterium and fluorine atoms intersecting at the surface of photoresist samples. We present experimental evidence that the etch yield of photoresist (carbon atoms removed per incident argon ion) under these conditions is high compared to that of silicon and silicon dioxide. The presence of a simultaneous flux of deuterium atoms on the photoresist surface does not affect the etch yield despite the fact that DF is formed during the etching process. © 2000 American Vacuum Society. [S0734-2101(00)06405-8]

I. INTRODUCTION

It has long been accepted that the free fluorine radical concentration plays an important role in controlling the silicon dioxide to photoresist (PR) etch rate selectivity in fluorocarbon based etching plasmas. The addition of hydrogen has been shown to improve this selectivity, presumably by scavenging fluorine from the plasma reactor by forming HF. By reducing the fluorine to carbon ratio in the plasma and more specifically at the PR surface itself, the rate of polymer deposition increases causing the net PR etch rate to decrease. To develop reliable plasma models, it is necessary to understand the role of the fluorine radical and the other important neutral and ionic species present in the plasma in the PR etching process.

To simplify the investigation of this problem, one can decouple the gas phase chemistry from the surface chemistry by using a vacuum beam system. In these systems, one exposes a selected surface under vacuum (\(\sim 10^{-6}\) Torr) to relatively well-characterized and controlled beams of species, both neutral and ionic. Because this technique isolates each species, one can, in principle, determine the relative reactivity of all species studied. Vacuum beam studies have led to the development of phenomenological site balance models of the etching of silicon\(^1\)\(^-\)\(^6\) and silicon dioxide\(^7\)\(^-\)\(^8\) for a number of different chemistries relevant to practical etching plasmas. These models contain important physical parameters including sticking coefficients, etch product stoichiometries, and etch yields.

Previous work with photoresist etching has suggested that the vacuum beam approach may be useful for this material as well. It has been demonstrated that etching of organic polymers such as polymethylmethacrylate (PMMA) with an oxygen ion beam displays two regimes, an oxygen neutral limited regime at low pressure, and an ion limited regime at higher pressures.\(^9\) This same phenomenon has been observed in PR etching experiments in plasma reactors for SF\(_6\) plasmas as well as O\(_2\) plasmas with additives such as N\(_2\), CO, and NO.\(^10\)\(^-\)\(^12\) In these studies it was observed that at a constant ion flux, the etch rate of PR increased, and then eventually saturated as the relative concentration of oxygen and fluorine radicals, respectively, increased in the reactor. Each of these studies utilized a site balance formulation to explain the observations, but due to lack of knowledge of the exact composition and magnitude of the ion and radical fluxes, no quantitative modeling was attempted.

In this work, a vacuum beam system is applied to the study of photoresist etching kinetics. The complex chemistry of fluorocarbon and hydrogen containing plasmas is greatly simplified to facilitate study of the interaction of fluorine atoms and hydrogen atoms on the PR surface. This system is modeled with argon ions and independent fluxes of neutral deuterium and fluorine atoms coincident at the surface of a photoresist sample. From the results of these experiments, a phenomenological model of the photoresist etching process has been developed based on a site balance model. Separate experiments were conducted to measure the model parameters including the sticking coefficient, average etch product stoichiometry, and the physical sputtering yield of the photoresist.

II. EXPERIMENT

A. Main chamber and samples

The experimental apparatus consists of a differentially pumped, high vacuum chamber containing a rotatable carou-
FIG. 1. Schematic representation of the vacuum beam system. The sample carousel is mounted in the main chamber that has a base pressure of 1 \times 10^{-7}\ Torr. A quadrupole mass spectrometer (QMS) is mounted in the analysis section. It is separated from the main chamber by four stages of differential pumping and has a base pressure of 9 \times 10^{-10}\ Torr.

Samples include photoresist films deposited on a quartz crystal microbalance (QCM) substrate and a piece of solid quartz. The photoresist QCM is mounted on a copper block that holds the sample upright and exposes a circle 0.4 cm\(^2\) in area of photoresist to the ion and atom beams. The copper block maintains good thermal contact between the sample and the carousel so that the temperature can be controlled and measured. All etching experiments were performed at 13 °C ± 2 °C. The ion gun and the deuterium atom source are mounted on 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.

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Two positive tone photoresists, typical of those used in etching, were used in this series of experiments: Shipley System 805 (g-line) and Olin 10i (i-line). The photoresists were deposited via spincoating on QCM substrates to a thickness of approximately 1 μm and subsequently baked at 100 and 120 °C, respectively, for 20 min. By depositing the photoresist on QCM substrates, it was possible to make in situ, real time measurements of the PR etch rate by measuring changes in the QCM resonant frequency.\(^{13}\)

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. Species evolved or reflected from the sample surface can be detected, without suffering a gas phase collision, by a quadrupole mass spectrometer (QMS) mounted in the analysis section. 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. Modulated beam mass spectrometry was used to distinguish between the species originating at the surface and those coming from background gas.

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

The beam of atomic deuterium was created with an external plasma source mounted on the chamber. When the plasma is ignited, it extends down the length of the source’s inner quartz tube, dissociating the deuterium gas into D atoms. The D atoms from the plasma then effuse out of a hole at the tip of the tube into the vacuum chamber. The degree of dissociation was estimated to be 25% for these experiments (40% D atoms and 60% D\(_2\) molecules) using a method described previously.\(^{14}\) Deuterium was used in these experiments because detection of HF\(^+\) (mass to charge ratio = 20) is complicated by the presence of a peak in the QMS resulting from doubly ionized argon, Ar\(_2^+\) (also m/c = 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\(^+\) (m/c = 21) is not obscured by other species in the QMS, and therefore, DF generated at the PR surface can be detected.

Fluorine atoms are obtained from a separate plasma source. Fluorine gas flows through an alumina tube and the plasma is ignited in the tube. Atomic fluorine effuses into the vacuum chamber through a 1-mm-diam aperture at the end of the tube. The average degree of dissociation achieved in these experiments was 30%. The calibrations performed to determine the absolute fluorine and deuterium fluxes from the two atom sources are described elsewhere.\(^{14}\) The fluorine atom flux was varied from 0 to 6 \times 10^{15}\text{atoms/cm}^2\text{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}\text{atoms/cm}^2\text{s} by a similar procedure.

The argon ion flux, with ion energies of either 500 or 1000 eV, was obtained from a commercial ion gun (Physical Electronics). A range of Ar\(^+\) ion fluxes from 5 \times 10^{12} to 5 \times 10^{13}\text{ions/cm}^2\text{s} was used. Fluorine/argon ion flux ratios from 0 to 800 were obtained in these experiments 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.

III. PHOTORESIST ETCHING AND SINGLE RADICAL MODELING

A. Physical processes

The etch yield of photoresist as a function of the fluorine atom to argon ion flux ratio can be well represented by a simple phenomenological model. Three physical and chemical processes are incorporated into this model: chemisorption of fluorine on open sites on the photoresist surface, ion-assisted chemical sputtering of CF\(_x\) species, and physical sputtering of carbon from the photoresist. Spontaneous etching of the photoresist by fluorine radicals in the absence of ion bombardment was not detected during these experiments, and thus was not included in the model. This is not a surprising result as fluorine radicals alone have been demonstrated previously to be unable to etch photoresist.\(^{15}\) Fluorine
atom recombination to form fluorine molecules (F₂) was not detected, and therefore was also not included in the model.¹⁴

The mechanism used in the etching model is given below:

\[ x_F = x_F + \alpha_F F_{(ab)}, \]  

Chemisorption \( F_g + \alpha_F^* \rightarrow F_{(ab)} \), \( \text{Chemical sputtering} \ C_{(s)} + x F_{(ab)} \rightarrow C_F x_F + x \alpha_F^* \), \( \text{Physical sputtering} \ C_{(s)} \rightarrow C_{(g)} \). \( \text{The parameters in the mechanism are defined as follows:} \)

1. Controlled variables

\( \Gamma_F = \text{Fluorine flux (atoms/cm}^2/\text{s)} \) to the photoresist, \( J_{Ar^+} = \text{Argon ion flux (ions/cm}^2/\text{s)} \) to the photoresist.

2. Measured fitted parameters

\( s = \text{Sticking probability of a fluorine atom on an open photoresist surface site,} \)

\( Y_{Ph} = \text{Physical sputtering yield of carbon from the PR (atoms/ion),} \)

\( Y_{Ch} = \text{Ion-assisted chemical sputtering yield of CF}_x \text{ species from the PR (atoms/ion),} \)

\( x = \text{Number of fluorine atoms bonded to each chemically sputtered carbon atom,} \)

\( \alpha_F^* = \text{Total number of active sites per unit area,} \)

\( \theta_F = \text{Fractional fluorine coverage of the active sites on the PR.} \)

Note: Etch rates of PR are measured in amu/ion. To determine the etch yield of the PR, the measured amu/ion was converted to atoms/ion by assuming that the resist is mostly carbon and, therefore, the average resist atomic weight is 12 amu/atom.

The relative rates of the first two processes govern the surface coverage of fluorine on the PR. The equations describing these rates are as follows:

Fluorine chemisorption rate \( s = \Gamma_F (1 - \theta_F) \), \( \text{Chemical sputtering} \ C_{(s)} + x F_{(ab)} \rightarrow C_F x_F + x \alpha_F^* \), \( \text{Physical sputtering} \ C_{(s)} \rightarrow C_{(g)} \). \( \]

Table I. Parameters for the phenomenological model for photoresist etching with Ar⁺ ions and neutral fluorine and deuterium atoms. Parameter values shown in bold italics were adjusted to obtain the model fits. All other parameters were measured or inferred from scaling laws.

<table>
<thead>
<tr>
<th>Model parameters</th>
<th>Olin i-line</th>
<th>Olin g-line</th>
<th>Shipley i-line</th>
<th>Shipley g-line</th>
</tr>
</thead>
<tbody>
<tr>
<td>500 eV Ar⁺</td>
<td>3</td>
<td>0.25</td>
<td>0.1</td>
<td>0.14</td>
</tr>
<tr>
<td>1000 eV Ar⁺</td>
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<td>1.0</td>
<td>0.8</td>
<td>0.8</td>
</tr>
<tr>
<td>X_F</td>
<td>2.2</td>
<td>3</td>
<td>1.9</td>
<td>3</td>
</tr>
<tr>
<td>Y_Ch</td>
<td>23</td>
<td>32</td>
<td>37</td>
<td>53</td>
</tr>
</tbody>
</table>

FIG. 2. Etch yield (carbon atoms removed per incident argon ion) Shipley System 805 g-line photoresist as a function of the fluorine atom/argon ion flux ratio to the surface for 500 and 1000 eV Ar⁺ ions. Lines represent fits to a phenomenological model described in the text. Note that the etch yield seems to saturate at high fluorine atom to argon ion flux ratios.

Loss rate of fluorine due to chemical sputtering

\( = J_{Ar^+} Y_{Ch} \tag{5} \)

To obtain an expression for the etch yield as a function of the fluorine atom to argon ion flux ratio, the steady state coverage of fluorine on the surface must be determined. This can be accomplished, as is shown below, by using Eqs. (4) and (5) to solve for the fluorine coverage as a function of this ratio:

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

\[ \theta_F = \frac{s(\Gamma_F/J_{Ar^+})}{s(\Gamma_F/J_{Ar^+}) + x Y_{Ch}}. \]

This coverage is then used to determine the etch yield as a function of the neutral to ion flux ratio \( \Gamma_F/J_{Ar^+} \). The total carbon etch yield, shown in Eq. (8), is taken to be the sum of a physical component due to physical sputtering by argon ions alone and a chemical component due to the synergistic interaction of the fluorine atoms and the argon ions on the PR surface. The relative weight of these two components is determined by the fluorine coverage on the PR surface.

\[ EY_{\text{tot}} = Y_{Ph} (1 - \theta_F) + Y_{Ch} \theta_F. \]

Substituting Eq. (7) into Eq. (8) we obtain

\[ EY_{\text{tot}} = Y_{Ch} + (Y_{Ch} - Y_{Ph}) \frac{s(\Gamma_F/J_{Ar^+})}{s(\Gamma_F/J_{Ar^+}) + x Y_{Ch}}. \]

B. Etch yield (Ar⁺/F)

Figures 2 and 3 show the etch yield of Olin i-line and Shipley g-line PR, respectively, with 500 and 1000 eV argon ions in the presence of a fluorine atom flux. The etch yields of both PRs exhibit a neutral flux limited and an ion flux limited regime as the ratio of these fluxes is varied from 0 to
Sputtering of several C atoms and the sputtering of more than 20 CF molecules may in fact be the etching of long chain molecules. Thus, what appears to be sputter etching of the photoresist surface may consist of an interwoven network of fluorine atoms compared to silicon. Since carbon atoms tend to polymerize, the etch rate of fluorocarbon layers deposited on silicon is much more sensitive to the increase observed in those systems.  It is possible that these large etch yields for photoresist are a result of a different character for carbon bonding as compared to silicon. Carbon atoms tend to polymerize, the photoresist surface may consist of an interwoven network of long chain molecules. Thus, what appears to be the sputtering of more than 20 CF molecules, may in fact be the sputtering of several CmFm molecules ($m \approx 2$). Sputtering of long carbon chains from surfaces has been observed in molecular dynamics simulations of the ion bombardment of fluorocarbon layers deposited on silicon.

The following procedure was used to obtain the model parameters. The values of these model parameters are listed in Table I. First, the physical sputtering yield ($Y_{\text{ph}}$) of each PR was measured for both the 500 and 1000/eV cases. This was done by performing etching experiments with $\Gamma_{\text{F}}/J_{\text{Ar}^+} = 0$ for both ion energies. Next, $x$, the etch product stoichiometry was calculated for both 500 and 1000 eV using data from the QMS, and found to be approximately 1. The QMS data were then used to determine $s$, the fluorine bare site sticking probability, at both 500 and 1000 eV. The sticking probability was found to scale with the square root of the ion energy for the Olin resist, consistent with previous results. With $x$ and $s$ defined, the phenomenological model was then fit to the 1000 eV data set by adjusting only $Y_{\text{ch}}$, the ion-assisted chemical sputtering yield for carbon. To obtain the 500 eV curve, the chemical sputtering yield was assumed to be proportional to the square root of the ion energy. This scaling is observed for many ion driven etch processes.

Thus, only one parameter ($Y_{\text{ch}}$ at 1000 eV) was fit to the photoresist etch yield data to obtain model predictions of the etch yield data at both 500 and 1000 eV.

### C. Etch product stoichiometry and sticking probability

The etch product stoichiometry and the F atom sticking probability on PR in these experiments were estimated using modulated beam mass spectrometry. In the absence of ion bombardment, F atoms will physisorb to the PR surface and desorb without reacting, essentially “reflecting” from the surface. This reflected flux of F atoms can be monitored in the QMS as a signal at mass 19. However, when ion bombardment is initiated, the mass 19 signal decreases. This decrease corresponds primarily to the amount of F consumed in the etching process. Although there are many different chemical species present in the stream of etch products, their average stoichiometry can be determined by quantifying the decrease in the reflected F flux from PR surface ($\Delta \Gamma_F$). If we assume that the physical sputtering rate of F is small compared to its chemical removal rate as CF$_x$ species, then we can attribute this decrease solely to F containing etch products. This assumption is reasonable because the physical sputtering yield of carbon is almost an order of magnitude smaller than its chemical sputtering yield. Therefore, it is likely that the physical sputtering yield of F only contributes to a small error of $\approx 10\%$ in the value of $x$. The decrease in the F flux, combined with the etch rate obtained from the QCM ($\Gamma_{\text{C}}$), yields the number of F atoms removed per carbon atom etched

$$x = \frac{\Delta \Gamma_F}{\Gamma_{\text{C}}} \left( \frac{\text{Fluorine flux data from QMS}}{\text{Etch rate data from QCM}} \right). \quad (10)$$

This value, determined for a range of $\Gamma_F/J_{\text{Ar}^+}$ flux ratios for etching with 500 and 1000 eV ions, was approximately one fluorine atom per carbon atom for both resists. The data for the Olin resist are presented in Fig. 5. The low degree of fluorination (i.e., CF$_x$ where $x < 2$) of the PR etch products is significant, as these species are likely to have a high sticking probability, contributing to film deposition on surfaces in a
reactor. These etched products could also have a significant impact on the composition of the plasma itself.

The bare site sticking probability for fluorine atoms can also be inferred from the decrease in the reflected fluorine flux during the etching process. The F sticking probability is simply the number of F atoms in the incident beam that adsorb to the PR during etching ($\Delta \Gamma_F$), divided by the total number of atoms in the beam ($\Gamma_F$). Since the $\Delta \Gamma_F$ measurement is made during the etching process where the F coverage is nonzero, the measured sticking coefficient is weighted by the fraction of open sites available for adsorption ($1 - \theta_F$). Thus, the bare site sticking probability ($s$) is

$$s[1 - \theta_F] = \frac{\Delta \Gamma_F}{\Gamma_F}. \quad (11)$$

However, since the F coverage must be predicted by the model, several iterations are required to determine $s$.

Figure 5 shows the values calculated for the bare site sticking probability of F atoms on the Olin PR over a range of $\Gamma_F/\Gamma_{Ar^+}$ flux ratios at 1000 eV. It is clear from the figure that, as expected, the bare site sticking probability is not a function of the fluorine atom/argon ion flux ratio. This is important because if the sticking probability were a function of coverage, the expression for the rate of adsorption of fluorine from the gas phase would need to be much more complicated.

Dissociative ionization of CF$_x$ etch products in the QMS which leads to an increase in the measured F$^+$ signal can lead to an underestimate of both $x$ and $s$. However, the cross section for ionization in the QMS favors ionization of the carbon-containing fragment (i.e., CF$_x$ + e$^- \rightarrow$ CF$_{x-1}^+$ + F + 2e$^-$) much more than dissociative ionization yielding a fluorine ion. In addition, fluorine ions produced by dissociative ionization tend to be more energetic than those which are formed from the parent F atom. These daughter F ions have a lower detection efficiency in the QMS, and therefore their contribution to the overall F atom signal is less than for the direct ionization of F atoms. Thus, dissociative ionization can be ignored in this calculation.

**Fig. 6.** Olin photoresist etch yield as a function of the fluorine atom/argon ion flux ratio. Two cases are presented, one with and one without a simultaneous flux of deuterium atoms to the surface. As is evident from these figures, even in the presence of a deuterium flux that is more than four times the flux of fluorine, the etch yield of the resist is unaffected by the D atom flux. The line represents a fit to a phenomenological model described in the text.
tered [see Eq. (8)]. However, within the limits of detection for this apparatus, the etch yield of the photoresist is unaffected by the presence of a simultaneous flux of D atoms to the surface. This is despite an excess of D radicals striking the surface resulting from flux ratios of D to F atoms ranging from 1 to 20. Since the etch yields of PR with fluorine and deuterium are identical to those without deuterium, the surface coverage of fluorine in each case must be nearly identical. This indicates that the reaction rate between the D and F radicals on the surface is very small under these conditions. This observation is confirmed by the QMS measurements. In the presence of a flux of both F atoms and D atoms, the reflected F atom flux is only slightly lower than with no D present. This suggests that only a small percentage of the F atom flux (less than 1%–2%) is consumed in the surface reaction to form DF. There is no detectable difference in the fluorine molecule flux in the presence of D atoms.

To check the assumption that fluorine atoms are the key etchant species, the etch yield as a function of D radical and F₂ molecule fluxes were measured. Figure 8 shows that the etch yield enhancement of PR under similar fluxes of these chemical species is far less than for fluorine atoms. The contributions to the etch yield from fluorine molecules, atomic deuterium, and molecular deuterium have been neglected in the overall phenomenological model due to their relatively small impact on the etching yield, and the etch yield is taken to be only a function of the fluorine concentration on the PR surface.

IV. CONCLUSIONS

The etch yields of two photoresists, Shipley System 805 g-line and Olin 10i i-line photoresist, have been measured using independent beams of Ar⁺ ions, deuterium atoms, and fluorine atoms. The etch yield, measured in carbon atoms removed per incident ion, was observed to increase dramatically as the fluorine atom/argon ion flux ratio, \( \Gamma_F / J_{Ar^+} \), was increased until an eventual saturation in the etch yield was observed. This behavior is indicative of a transition from physical sputtering to chemical sputtering as the photoresist surface becomes saturated with chemisorbed fluorine. A phe-
nomenological model has been developed for these etching experiments. Several key parameters for this model such as the etch product stoichiometry, the physical sputtering yield, and the fluorine sticking coefficient have been independently measured for this system. The ion-assisted chemical etching yield of photoresist was determined by fitting this model to experimental data. The scaling of this yield from 500 to 1000 eV was found to be consistent with the assumed square root dependence on the ion energy of the etch yield.

It has also been shown that the photoresist etch yield does not change when the surface is simultaneously exposed to a flux of atomic deuterium and atomic fluorine during the etching process, even when the D flux is 20 times the F atom flux. This is true despite the formation of detectable quantities of DF on the PR surface during the etching process. This suggests that the direct abstraction of chemisorbed F atoms from the PR surface by hydrogen atoms is not a key process in reducing the fluorine to carbon ratio at the PR surface, and therefore does not contribute to a reduction in PR etch rate. Therefore, there must be other processes that are significant in reducing the fluorine content of these plasmas.

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