I. INTRODUCTION

Virtually all plasma etching processes for Si involve the formation of volatile Si–halide products.1–3 Fluorine-containing plasmas are usually avoided because, although high etch rates can be obtained, the fast chemical reaction with F atoms leads to undercutting of the mask and thus a loss of anisotropy.1–4 Cl atoms etch Si very slowly (except for n-type doped) in the absence of ion bombardment;5 while etching with Cl and Cl2 is greatly accelerated by ion bombardment.3,6 Consequently, Cl-containing plasmas are widely used for anisotropic etching of Si. Cl-containing plasmas do, however, have some disadvantages. Etched profiles often deviate from ideal vertical sidewalls, and selectivity with respect to etching of SiO2 and especially photoresist etch masks is often not as high as desired. Br-containing plasmas (e.g., HBr feed gas) have been reported to have superior anisotropy and selectivity for etching of Si.7–15 In general, etch rates are not as high as those in Cl2 plasmas, however, and consequently many etch processes have been developed with a mixture of Cl2 and HBr to simultaneously obtain high rates and selectivities, and nearly ideal anisotropy. The mechanisms by which simultaneous impingement by Cl, Br, and H-containing species affects the Si etch rate, etch profile, and selectivity are unknown.

Previously, we reported a technique for real-time detection of adsorbates during plasma etching in which laser-induced desorption (LD) was combined with laser-induced fluorescence (LIF) detection.16,17 Chlorine coverage was determined during etching of Si in high density, low pressure helical resonator plasmas of pure Cl2 and Cl2/O2 for a range of plasma conditions, using LD–LIF detection of SiCl. Coupled with x-ray photoelectron spectroscopy (XPS) after sample transfer under high vacuum, it was shown that Cl coverage scaled with the SiCl LD–LIF signal. The Cl coverage during etching was found to be about twice the saturated Cl coverage obtained by exposing Si to Cl2 in the absence of a plasma. The Cl coverage did not change appreciably after the plasma was extinguished and the gas was pumped away. At pressures above ~0.5 mTorr, the layer formed during etching reached saturated coverage on a time scale that was short compared to the etch rate. From the pressure, power, and direct current (dc) bias dependences we concluded that ion flux limits the rate of desorption of etch products, and therefore also the etch rate, even in these low pressure, high-charge-density plasmas.

In the present study, we extend the LD–LIF method to study Si(100) surfaces in real time during etching in mixed HBr/Cl2 plasmas. Cl and Br coverages were monitored by LD–LIF detection of SiCl and SiBr, respectively. XPS analysis was also performed after etching to measure Cl and Br coverages on Si(100), as well as on polycrystalline-Si (poly-Si) and photoresist surfaces.

Competitive halogenation of silicon surfaces in HBr/Cl2 plasmas studied with x-ray photoelectron spectroscopy and in situ, real-time, pulsed laser-induced thermal desorption

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Using x-ray photoelectron spectroscopy (XPS) and real-time, laser-induced thermal desorption–laser-induced fluorescence (LD–LIF), we have determined the coverage of Br and Cl on Si(100) surfaces that are etched in mixed HBr/Cl2 plasmas. Halogen coverages measured by XPS after etching are directly proportional to the fraction of the respective halogen in the feed gas. LD–LIF was detected from SiCl(g) and SiBr(g) products with intensities that are a semiquantitative measure of instantaneous Cl and Br coverages. Saturated coverages during etching in Cl2 and HBr plasmas are 1.0×1015 Cl/cm2 and 6.0×1014 Br/cm2, respectively. Etch rates at these two extremes are 2170 and 1330 Å/min, and therefore are proportional to the respective halogen coverages. It therefore appears that the rate of formation of volatile Si–halides, stimulated by ion bombardment, is lower for HBr mainly because less halogen is available on the surface at saturated coverage. Langmuir probe measurements indicate that the ion flux is 17% lower in pure HBr plasmas, compared with Cl2 plasmas at the same power. The plasma potential, direct current bias voltage, and hence ion energy were nearly constant, however, over the range of gas mixtures. The slightly different ion fluxes suggest that the ion bombardment-stimulated process, although similar for Cl2 and HBr plasmas, is actually slightly more efficient on a per halogen basis for Br versus Cl. Positive photoresist surfaces that were also exposed to the plasma differ from Si in that less Br adsorbs on the surface both in pure HBr and mixed HBr/Cl2 plasmas. Apparently the lower reactivity of photoresist with Br (compared with Cl) is at least partly responsible for the widely observed slower etch rate of photoresist in HBr plasmas, and hence enhanced selectivity when etching Si. © 1995 American Vacuum Society.

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II. EXPERIMENTAL PROCEDURE

The apparatus used in this study has been described in detail in recent publications.\textsuperscript{16–19} The helical resonator plasma reactor is connected to an ultrahigh vacuum (UHV) XPS analysis chamber by a high-vacuum sample transfer chamber. The discharge was operated with a mixture of HBr and Cl\textsubscript{2} at a total pressure of 2.1 mTorr [see Ref. 20(a) for a correction of pressures in previous studies] and at a constant total flow of 5.5 standard cubic centimeters per minute (sccm). The helical resonator source was operated at a radio frequency (rf) of 11.21 MHz and a net power of 280 W, and the substrate stage was biased with a second rf (14.5 MHz) source, to obtain a dc bias voltage of $-35$ V. Si(100) substrates ($n$ type, $P$ doped, 5–50 $\Omega$ cm) were cleaved into 1.5×1.5 cm pieces and clamped to a 1 in. diam. stainless steel sample holder that can be transferred under high vacuum from the etching chamber to the analysis chamber. The wafer temperature was measured directly by interferometric thermometry, as described elsewhere.\textsuperscript{18,19} The sample temperature, initially at 25 °C, increased to 130 °C in 3 min and then to $\sim200$ °C in 6 min. Most of the measurements reported here required that the plasma be on for $<3$ min. No changes in signals were observed that could be ascribed to heating of the wafer during longer plasma exposures.

During etching, the Si(100) surface was irradiated with laser pulses and laser-desorbed SiCl and SiBr products were detected by laser-induced fluorescence. The XeCl excimer laser (Lambda Physics model EMG 203, $\lambda=308$ nm) was operated at 5 Hz and delivered a fluence of 0.47 J/cm\textsuperscript{2} to the sample surface at normal incidence in a 2.6×6.2 mm rectangular beam. LIF was dispersed with a monochromator and detected with a GaAs photomultiplier tube. Lenses were used to image light from the near-surface region (0–4 mm above the surface) onto the entrance slit of the monochromator. A boxcar integrator with a 1 $\mu$s-wide gate was used to integrate over the signal pulse generated by the 15-ns-long laser pulse.

After etching and transfer of the sample to the analysis chamber, XPS analysis was performed on Si(100), undoped poly-Si, and photoresist surfaces. The photoresist was a positive resist (Shipley 1805) composed of 30 wt % novolac resin and 70 wt % 1-oxo-2-diazo-naphthoquinone-5-arylsulfonate sensitizer. The atomic composition of this mixture (excluding H) is: 83% C, 14% O, 2% N, and 1% S.

III. RESULTS

Typical Br(3$p$) and Cl(2$p$) XPS spectra are shown in Fig. 1 for Si(100) after etching with different HBr:Cl\textsubscript{2} ratios. As expected, both Br and Cl are adsorbed on Si(100) after etching in HBr/Cl\textsubscript{2} plasmas, and the XPS signal increases with increasing proportion of the respective halogen in the feed gas. Small Br(3$p$) and Cl(2$p$) signals in pure Cl\textsubscript{2} and HBr plasmas, respectively, are due to residual HBr (and possibly Br\textsubscript{2}) and Cl\textsubscript{2} desorbing from the walls of the chamber. XPS measurements performed on poly-Si surfaces (not shown in the figures, but included in Table I) were indistinguishable from the Si(100) results, as may be expected, since ion bombardment would likely make both these surfaces disordered.\textsuperscript{21}

LD–LIF spectra are shown in Fig. 2 for feed gas ratios spanning those used in the XPS measurements presented in Fig. 1. Background from scattered laser light has been sub-

![FIG. 1. XPS spectra of Cl(2$p$) and Br(3$p$) on Si(100), recorded after etching in HBr/Cl\textsubscript{2} plasmas. The top five spectra have their intensities offset for clarity. Br(3$p$) lines are presented here because they are close in binding energy to the Cl(2$p$) line. The Br(3$d$) line is used in subsequent analysis [Ref. 20(b)].](image-url)

### TABLE I. Etch rates and halogen coverages for etching of poly-Si and photoresist in HBr/Cl\textsubscript{2} plasmas. Cl and Br coverages are Cl(2$p$) and Br(3$d$).

<table>
<thead>
<tr>
<th>%HBr/100% Cl\textsubscript{2}</th>
<th>Etch rates ($\AA$/min)</th>
<th>Cl</th>
<th>Br</th>
</tr>
</thead>
<tbody>
<tr>
<td>0/100</td>
<td>2166</td>
<td>0.48</td>
<td>...</td>
</tr>
<tr>
<td>20/80</td>
<td>2498</td>
<td>0.40</td>
<td>0.045</td>
</tr>
<tr>
<td>100/0</td>
<td>1334</td>
<td>...</td>
<td>0.30</td>
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</tbody>
</table>

<table>
<thead>
<tr>
<th>%HBr/100% Cl\textsubscript{2}</th>
<th>Etch rates ($\AA$/min)</th>
<th>Cl</th>
<th>Br</th>
</tr>
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<tbody>
<tr>
<td>0/100</td>
<td>2320</td>
<td>0.50</td>
<td>...</td>
</tr>
<tr>
<td>20/80</td>
<td>1630</td>
<td>0.40</td>
<td>0.019</td>
</tr>
<tr>
<td>100/0</td>
<td>628</td>
<td>...</td>
<td>0.21</td>
</tr>
</tbody>
</table>
fluoresces. The emitter was previously identified as SiCl in a pure HBr plasma. The emitter is SiBr excited at 308 nm as a result of the transitions:

SiCl ($B^2\Sigma^+\leftarrow X^2\Pi_j$) ($\nu' = 0$) $\rightarrow$ SiCl($X^2\Pi_{3/2,1/2}$) ($\nu'' = 3, 4$). (1)

An analogous LD–LIF process occurs during etching of Si in a pure HBr plasma. The emitter is SiBr($B^2\Sigma^+\leftarrow X^2\Pi_j$) excited at 308 nm as a result of the transitions:

SiBr ($B^2\Sigma^+\leftarrow X^2\Pi_j$) ($\nu' = 0$) $\rightarrow$ SiBr($X^2\Pi_{3/2,1/2}$) ($\nu'' = 1 - 3$) (2)

Fluorescence from the excited state to the $\nu''$=0, 1 levels of the ground electronic state is readily identified in the top spectrum in Fig. 2, recorded during etching in a pure HBr plasma. LD–LIF spectra for mixed HBr/Cl₂ plasmas contain contributions from both SiBr and SiCl that scale with the fraction of the respective halogen in the feed gas, similar to the XPS spectra in Fig. 1.

The integrated XPS peak intensities for Cl(2p), Br(3d) and Cl(2p) + Br(3d) are presented in Fig. 3. The intensities are divided by XPS sensitivity factors and ratioed to the integrated Si(2p) peak intensity, which is also divided by its sensitivity factor. Consequently, relative coverages of Cl can be compared to those for Br by comparing the XPS intensities plotted in Fig. 3. The solid lines are linear least-square fits. The dashed lines are predicted dependences if Br and Cl compete equally for adsorption sites, in proportion to the halogen content of the feed gas. Top: SiCl ($\Delta$), SiBr ($\bigcirc$), and SiCl+SiBr ($\square$) LIF intensities [normalized to the corrected Cl(2p) and Br(3d) XPS intensities at 100% Cl₂ and HBr, respectively] vs % HBr. The open symbols refer to intensities derived from single peaks (2989 Å for SiCl and 3009 Å for SiBr), and the open, crossed symbols refer to signals derived from a least squares fit to a combination of spectra for pure Cl₂ and HBr plasmas. The curves, which are second- and third-order polynomial fits, are to guide the eye.

The XPS spectra in Fig. 1 show contributions from both SiBr and SiCl that scale with the fraction of the respective halogen in the feed gas, similar to the XPS spectra in Fig. 1.
tions” and the remaining three spectra for mixed HBr/Cl₂ plasmas were used in least square fits generated from a mixture of these two functions. The results of both methods of analysis are presented in Fig. 3. The agreement between the two methods is acceptable, indicating that the entire SiCl and SiBr spectra have the same dependence on %HBr. Although the SiCl and SiBr LD–LIF signals depend on %HBr in a manner that is qualitatively similar to the Cl(2p) and Br(3d) XPS signals, the SiBr signal (normalized to the Br–XPS signal at 100% HBr) drops below the Br coverage measured by XPS for mixed HBr/Cl₂ plasmas. Conversely, the SiCl LD–LIF signal (normalized to the Cl–XPS signal for pure Cl₂ plasmas) is higher on average than the Cl XPS coverage after etching in HBr/Cl₂ mixtures. The total SiBr₃+SiCl LD–LIF signal is, however, in agreement with the total Br+Cl coverage determined from XPS.

The time dependence and stability of the SiBr₃ adsorbed layer after etching in a HBr plasma (Fig. 4) was investigated in the same manner as that reported previously for the SiCl₃ layer after etching in a Cl₂ plasma. After the steady-state signal was established during etching, the plasma was turned off while the laser continued to irradiate the surface (● in Fig. 4). The signal immediately (with 1 laser pulse) dropped by a factor of 2 and then decayed by another ~30% over the next 20 laser pulses. The steady-state signal level with no plasma is about one-fourth of the intensity observed during plasma exposure, and indicates a significant amount of laser-induced etching. The trend is reversible, as shown by the open square symbols.

In another experiment, steady-state plasma etching is established, the laser is blocked before the plasma is extinguished, the gas is pumped away, and the laser is unblocked. The signal on the first laser pulse is equal to the steady-state signal after the plasma is extinguished. Consequently, surface analysis carried out after etching and then transferring the sample to the analysis chamber under vacuum is representative of the surface that was present during etching. A similar observation and conclusion have been made for the layer present during and after exposure to HBr with the plasma off (▲ in Fig. 4). All of these time-dependent results are analogous to observations for the SiCl₃ layer formed by etching Si in a Cl₂ plasma.

Etch rates for poly-Si and photoresist were determined for pure Cl₂ and HBr plasmas, and for one mixture (20%HBr/80%Cl₂). These results are summarized in Table I, along with XPS measurements of Cl and Br coverages (normalized to the major component of the underlying material).

Previous Langmuir probe measurements of pure Cl₂ plasmas indicated that the positive ion flux was $4\times10^{16}$ cm⁻² s⁻¹, and the plasma potential was 50 V. These measurements were reproduced in the present study, and additional measurements of mixed HBr/Cl₂ plasmas indicated that the ion flux fell by 17% between pure Cl₂ and 50% HBr/50%Cl₂ and then remained constant as the percentage of Cl₂ was further reduced. The plasma potential was constant to within 5 V over the range of gas mixtures.

IV. DISCUSSION

The saturated coverage of Cl, $\theta_{Cl}^0$, measured by XPS after etching Si in a Cl₂ plasma was previously estimated to be $1.0\times10^{13}$ cm⁻². Based on the Cl-to-Br XPS ratio of 1.6:1 measured in the present study, we therefore estimate that the saturated Br coverage ($\theta_{Br}^0$) is $6.0\times10^{14}$ cm⁻² after etching in HBr plasmas. The lower Br coverage is likely due in part to site blocking by coadsorbed H. Although we could not determine H coverages in this study, H atoms are present in the discharge and therefore are expected to adsorb on the surface during etching. In addition, adjacent adsorption sites could be blocked by the larger Br atom (atomic radii of Cl and Br are 0.97 and 1.12 Å, respectively). This steric hindrance is expected to be more effective in suppressing di- and trihalide species that form during plasma etching and is consistent with observations (SiCl:SiCl₂:SiCl₃ = 1.0:0.84:0.25, (SiBr:SiBr₂:SiBr₃ = 1.0:0.78:0.17).

The dashed curves in Fig. 3 represent a simple model in which the halogen coverage is assumed to be proportional to the fraction of the respective halogen, $f_{Br}$, and $f_{Cl}$ in the feed gas, defined as

$$f_{Br} = \frac{p_{HBr}}{p_{HBr}+2p_{Cl_2}}.$$  

and

$$f_{Cl} = \frac{2p_{Cl_2}}{p_{HBr}+2p_{Cl_2}},$$

where $p_{HBr}$ and $p_{Cl_2}$ are the partial pressures of HBr and Cl₂.

In addition, it is assumed that Br (plus any adsorbed H) occupies 1.6 times as many sites as Cl. This steric hindrance is expected to be more effective in suppressing di- and trihalide species that form during plasma etching and is consistent with observations (SiCl:SiCl₂:SiCl₃ $f_{Br} \approx 1.0$ for pure Cl₂, $f_{Cl} \approx 0.78$ for pure Cl₂).

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where $p_{HBr}$ and $p_{Cl_2}$ are the partial pressures of HBr and Cl₂. In addition, it is assumed that Br (plus any adsorbed H) occupies 1.6 times as many sites as Cl (the ratio of the reciprocals of the Br and Cl XPS coverages, $\theta_{Br}^0$ and $\theta_{Cl}^0$, determined from pure HBr and Cl₂ experiments) for all gas ratios, and that the surface is always saturated coverage during (and after) etching. So

$$\theta_{Cl}^0 \approx \frac{1.6\theta_{Br} + \theta_{Cl}}{0.6f_{Br}},$$

where $\theta_{Br}$ and $\theta_{Cl}$ are the halogen coverage for etching in mixed HBr/Cl₂ plasmas. Therefore

$$\theta_{Br} = \frac{\theta_{Cl}^0 f_{Br}}{1 + 0.6f_{Br}}.$$
The halogen coverages $\theta_{\text{Br}}$, $\theta_{\text{Cl}}$, and $\theta_{\text{Br}}+\theta_{\text{Cl}}$ computed from Eqs. (5) and (6) are plotted as the dashed lines in Fig. 3. Within the scatter of the data they provide good fits, indicating that the coverages determined by XPS for either halogen are simply proportional to the percentage of that halogen in the feed gas.

Contrary to the XPS data, when the LD–LIF signals are normalized to the XPS data at 0% and 100% HBr, for mixed HBr/Cl$_2$ plasmas the SiBr LD–LIF signal falls below the near-linear dependence on %HBr and Br (XPS) coverage, while the SiCl LD–LIF signal lies above the near-linear dependence on %Cl$_2$ and Cl (XPS) coverage. Either Br displaces Cl in the short period following etching, before the etching chamber is evacuated and the sample transferred to the analysis chamber, or the LD–LIF signals are not precisely proportional to the respective halogen coverages during etching.

To investigate the likelihood of Cl displacement by Br after plasma etching, the following additional measurements were performed. The Si sample was etched in a pure Cl$_2$ plasma for several minutes. The plasma was then extinguished and the Cl$_2$ pumped away. The reactor was then filled with HBr to a pressure of 2.1 mTorr for 1 min. The HBr was then pumped away and the sample was transferred to the XPS chamber. The Br coverage was only slightly higher than the trace amount observed after simply etching in a pure Cl$_2$ plasma, indicating that displacement of adsorbed Cl by Br from exposure to HBr, does not occur to any appreciable extent. The converse is also true; Cl does not displace adsorbed Br after etching in an HBr plasma and then exposing the sample to Cl$_2$.

Therefore, the relative halogen coverages measured by XPS after etching are expected to be close to those present during etching, and the LD–LIF signals deviate somewhat from these coverages. The dependence of the SiBr LD–LIF signal on Br XPS coverage could simply indicate that the relative yield of the SiBr laser-induced thermal desorption (LITD) increases as Br coverage increases, perhaps due to a weakening of the surface binding energy from repulsive adsorbate-adsorbate interactions. Previously we showed that the SiCl LD–LIF signal scaled linearly with Cl coverage measured by XPS when Cl coverage was changed from half of saturated coverage to saturated coverage. Consequently, as the surface reaches its peak temperature where desorption of SiBr is expected to be most favored, the Br coverage would drop and so the yield of desorbed SiBr would decrease. Conversely, adsorbed Br could hinder formation and prompt desorption of SiCl during the laser pulse, thereby enhancing the SiCl yield by providing more adsorbed Cl at the peak temperature. Regardless of the explanation for the small differences between the Si–halide LD–LIF signals and halogen coverages measured by XPS, the LD–LIF signals provide an instantaneous measure of Cl and Br coverages, which are accurate to within a factor of 1.7 for Br and 1.3 for Cl.

Because halogen coverage is proportional to the fraction of halogen in the feed gas, the overall rate of bromination in HBr plasmas, which is a function of the sticking coefficients and partial pressures of HBr, Br$_2$, and Br-containing ions, must be nearly equal to the rate of chlorination in Cl$_2$ plasmas, which likewise depends on Cl$_2$, Cl, Cl$^+$, and Cl$^{2+}$ sticking coefficients and partial pressures. Since it was shown previously that Si etching in a Cl$_2$ plasma is limited by ion bombardment and not by chlorination of the surface, it then follows that Si etching in an HBr plasma operated under the same conditions is also limited by ion bombardment because the etch rate with HBr is slower than that with Cl$_2$. The ratio of the etch rate in HBr plasmas to that in Cl$_2$ plasmas (0.61, Table I) can be compared with the ratio of the respective halogen coverages measured after etching with these gases (0.60) and to the ratio of the respective ion fluxes (0.83), measured with the Langmuir probe. This comparison suggests that HBr plasmas etch Si more slowly than do Cl$_2$ plasmas mainly because less halogen is present on the surface at saturated coverage and, hence, the ion-enhanced rate of formation of volatile products such as SiBr$_2$ is lower. Since the ion fluxes are somewhat lower in HBr plasmas, the process is, however, slightly more efficient for Br on a per-halogen basis (i.e., the ratio of etch rates would be 0.83...


$x \times 0.60 \approx 0.50$ if Br and Cl were equivalent). Apparently, the 20% HBr/80% Cl\textsubscript{2} measurements deviate somewhat from this simple scaling relationship. Relative to a pure Cl\textsubscript{2} plasma, the total halogen coverage is $\sim 5\%$ lower and the ion flux is $\sim 10\%$ lower, yet the etch rate is 15% higher. While within the combined uncertainties of these measurements, secondary effects from the presence of coadsorbed H, differences in ion composition and mass, and reactions occurring in the gas phase or on the walls of the reactor could play a small role in enhancing the Si etch rate when smaller amounts ($\sim 20\%$) of HBr are added to Cl\textsubscript{2} plasmas.

Saturated chlorine coverage on photoresist surfaces is about the same as on poly-Si (Table I). Bromination in HBr-containing plasmas is different, however, in that Br coverage is less on photoresist surfaces than on Si. The Br coverage after etching photoresist in a pure HBr plasma is less than half the Cl coverage found after etching in a Cl\textsubscript{2} plasma (Table I). Likewise, for a mixture of 20% HBr/80% Cl\textsubscript{2}, the Br/Cl ratio is only 0.047 on photoresist, compared to 0.11 on poly-Si. Apparently, the reduction of the etch rate of photoresist with addition of HBr to the plasma is not due to the formation of a protective brominated layer. Preferential formation of a brominated carbon layer may have been anticipated from the low vapor pressure of CBr\textsubscript{3} vs CCl\textsubscript{4}. Nor is it due to the formation of an SiO\textsubscript{2} film in the absence of added oxygen. Instead, it is likely that Br simply reacts more slowly with the photoresist in the presence of ion bombardment, relative to H and Cl. This is consistent with the C–X bond strength (X=Br, Cl, or H) in the series CH\textsubscript{3}Br:CH\textsubscript{3}Cl:CH\textsubscript{4}=68:81:102 kcal/mol.\textsuperscript{36,37} In addition, H atoms formed in the plasma will replenish H lost from the surface of the polymer, and could reduce its etch rate by Br and Cl, in a mechanism analogous to the slowing of the etch rate of SiO\textsubscript{2} by the addition of O\textsubscript{2} to the plasma.

V. CONCLUSIONS

X-ray photoelectron spectroscopy and real-time laser desorption-induced fluorescence were used to study Si(100) surfaces after and during etching in HBr/Cl\textsubscript{2} high-density, low-pressure helical resonator plasmas. As found previously for Cl coverage on Si in Cl\textsubscript{2} plasmas, the Br coverage on Si, sensed by SiBr LD–LIF, did not change appreciably after the HBr plasma was extinguished and the HBr pumped away, indicating that postetching XPS analysis is indicative of the surface during etching. Br and Cl coverages on Si increase linearly with the percentage of HBr and Cl\textsubscript{2}, respectively, in the feed gas. The Cl coverage is $1.0 \times 10^{15}$ cm\textsuperscript{–2} after etching in a pure Cl\textsubscript{2} plasma, while the Br coverage is $6.0 \times 10^{14}$ cm\textsuperscript{–2} after etching in an HBr plasma. The lower saturation coverage for Br can be ascribed to its larger atomic radius and the presence of coadsorbed H. Etch rates in pure Cl\textsubscript{2} plasmas are 1.6 times higher than those in HBr plasmas, in proportion to the saturated coverages of Br and Cl. These results suggest that HBr plasmas etch Si more slowly than do Cl\textsubscript{2} plasmas mainly because less halogen is available on the surface for formation of volatile SiBr\textsubscript{x} products in ion bombardment-stimulated reactions. The slightly lower ion fluxes in HBr plasmas, compared to Cl\textsubscript{2} plasmas at the same power and bias voltage, indicate that, although similar, the yield of the ion bombardment process is slightly more efficient on a per halogen basis for Br than for Cl.

The etching behavior of poly-Si is the same as Si(100). However, photoresist differs in that Br is two to three times less likely to adsorb on it than on Si vis-à-vis Cl. Apparently this at least partly explains the improvement in selectivity of Si etching relative to photoresist when HBr is added to a Cl\textsubscript{2} plasma. A further reduction in photoresist etch rate could be caused by hydrogenation from H atoms formed in the plasma, compensating for H lost from the resist surface as a result of ion bombardment and reactions with Cl and Br atoms.

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\textsuperscript{(a) Due to a pressure drop that was not properly accounted for, the pressure of 1.0 mTorr given in previous studies (Refs. 16–18) was actually the same as the correct pressure of 2.1 mTorr used in this study. Similarly, the quoted pressures below 1.0 mTorr in Ref. 17 should be multiplied by 2, while those above $\sim$5 mTorr are correct. (b) Br(3d) was used, rather than Br(3p) because its spin-orbit splitting is smaller, resulting in a sharper peak. In addition, the baseline is flatter in the Br(3d) region. A loss feature associated with Si(2s) overlaps with the Br(3p) lines, making an accurate peak integration difficult. The 15% higher apparent Br coverages calculated using the Br(3p) peaks can be mostly attributed to this artifact.}


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