Effect of N$_2$O plasma treatment on the stabilization of water absorption in fluorinated silicon-oxide thin films fabricated by electron-cyclotron-resonance plasma-enhanced chemical-vapor deposition

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The variation of residual stress with the water absorption was reduced drastically by the N$_2$O plasma treatment for fluorinated silicon-oxide thin films. Fourier transformed infrared spectroscopy analysis showed that the film was oxidized by the plasma treatment. It was also determined that the oxidation occurred on the film surface from the P-etch rate and x-ray photoelectron spectroscopy analysis. The experimental results show that the stabilization results from the oxidation of the surface by the N$_2$O plasma treatment. © 2002 American Institute of Physics. [DOI: 10.1063/1.1458528]
to Park et al., the magnitude of the compressive stress increases with the water absorption for SiO\textsubscript{2} films deposited by PECVD.\textsuperscript{11} Haque, Naseem, and Brown insisted that three factors effect the variation of the residual stress in the case of SiO\textsubscript{2} films: water adsorption on the surface, Si—OH formation, and the interaction between adsorbed water dipoles in the columnar structure.\textsuperscript{12} We have previously reported that the SiOF films fabricated by ECR PECVD also show an increase of compressive stress with the water absorption, which results from the physical adsorption of water on the film surface.\textsuperscript{5} In this study, the amount of the water absorption was estimated by measuring the variation of the residual stress in films with the storage time in room air. The etching rate was determined in P-etch solution. All the analyses were carried out immediately after the plasma treatment process.

All the films were under compressive stress conditions (Table I). The compressive residual stress increases with the storage time in room air [25°C and 45% relative humidity (RH)], however that of SiO\textsubscript{2} film does not change (~−270 MPa). It is inferred that the SiO\textsubscript{2} films deposited in this study are very stable to water. Chang et al. also observed that ECR SiO\textsubscript{2} even deposited at room temperature did not absorb water and swell.\textsuperscript{5} Figure 1 shows the increment of compressive stress with respect to an initial stress value (\(\sigma_{i}\)), \(\frac{\sigma - \sigma_{i}}{\sigma_{i}}\) (%), as a function of storage time. The increment decreases significantly with increasing the plasma treatment time. Finally, the change of residual stress becomes negligible. These results indicate that the N\textsubscript{2}O plasma treatment effectively suppresses the water absorption of SiOF films. The inhibition of the water absorption by the plasma treatment has been reported previously, however an origin is not known. In order to clarify the reason of stabilization, the change of chemical bonding structure was analyzed using FTIR.

The variations of Si—O and Si—F peaks with the plasma treatment time are plotted in Fig. 2. The intensity of Si—O stretching mode (~1070 cm\textsuperscript{-1}) increases, while that of Si—F stretching mode (~945 cm\textsuperscript{-1}) decreases with the treatment time. The integrated intensities of Si—O and Si—F stretching peaks \(\frac{I_{Si-O}}{I_{Si-F}+I_{Si-O}}\) were used to estimate the fluorine content in the film. \(\frac{I_{Si-F}}{I_{Si-O}+I_{Si-F}}\) ratios are also summarized in Table I. The result implies that the plasma treatment removes the Si—F bonds and enhances the formation of Si—O bonds. It is thought that the energetic oxygen ions or radicals react with the films. It has been known that the water absorption in SiOF films is due to the interaction between the water molecules and Si—F bonds.\textsuperscript{3,4,7} Thus, it is supposed that the reduction of Si—F bond and formation of Si—O bond might have caused the stabilization of SiOF films. Researchers have already presented similar explanations about the effect of plasma treatment on SiO\textsubscript{2} and SiOF films.\textsuperscript{8–10} They explained that the surface state was changed after the treatment because of the ion bombardment or the oxidation. However, there is little experimental evidence that supports the change of surface clearly.

<table>
<thead>
<tr>
<th>Plasma treatment time (min)</th>
<th>Initial stress, (\sigma_{i}) (MPa)</th>
<th>(\frac{\sigma - \sigma_{i}}{\sigma_{i}}) (%) after 5 h in 45% RH air</th>
<th>(\frac{I_{Si-F}}{I_{Si-O}+I_{Si-F}}) (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>−70.0</td>
<td>100.2</td>
<td>10.9</td>
</tr>
<tr>
<td>1</td>
<td>−115.5</td>
<td>23.8</td>
<td>9.4</td>
</tr>
<tr>
<td>2</td>
<td>−115.4</td>
<td>9.2</td>
<td>8.3</td>
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<tr>
<td>3</td>
<td>−93.0</td>
<td>5.9</td>
<td>6.9</td>
</tr>
<tr>
<td>4</td>
<td>−90.8</td>
<td>−2.6</td>
<td>6.3</td>
</tr>
<tr>
<td>SiO\textsubscript{2}</td>
<td>−270.0</td>
<td>0.4</td>
<td>0</td>
</tr>
</tbody>
</table>
The film thickness was measured as a function of etching time in P-etch solution and the results are shown in Fig. 3. It has been well known that P-etch rate of silicon oxide film is very sensitive to the film density. The etching rate of SiO$_2$ in this study is $\sim 3$ Å s, which is a similar value for thermally grown SiO$_2$ ($\sim 2$ Å/s).$^{13}$ In the case of SiOF film without the N$_2$O plasma treatment, the etch rate is $\sim 40$ Å/s. Figure 3 indicates that the etching rate of the surface region ($\sim 200$ Å) is quite different from that of the bulk region for SiOF films after the N$_2$O plasma treatment. Although, the etching rate of bulk region remains nearly constant even after the N$_2$O plasma treatment, the etching rate of surface region decreases with increasing the plasma treatment time. It finally reaches to the value of SiO$_2$ film that does not absorb the water as presented in Fig. 1. It is expected that the surface region fully changed to dense silicon-oxide from SiOF by ions or radicals in the N$_2$O plasma for 4 min. However, there is another possible explanation that the slow etch rate of the surface is due to the densification of the surface region only by the ion bombardment without the oxidation. To clarify that oxidation occurs at the surface region, the elemental composition depth profile was obtained from XPS analysis and cross sectional view of SiOF film was observed using scanning electron microscopy (SEM).

Figure 4 shows the XPS depth profile results and cross sectional SEM images of SiOF films before [(a) and (b)] and after [(c) and (d)] N$_2$O plasma treatment for 4 min. XPS depth profile result was obtained after the sputtering process for 30 s to remove the contaminant on the film surface. The result shows that the plasma treatment removes the fluorine atoms on the film surface and changes the surface region to silicon oxide. Considering the change of $I_{Si-F}/(I_{Si-O}+I_{Si-F})$ (Table I) and XPS result, it is thought that the oxidation occurs in the surface region. XPS results also show no incorporation of nitrogen in the films, which implies that no reaction occurred between SiOF film and nitrogen atom. The cross sectional SEM image shows a layer with different brightness for the plasma treated film. It seems that the bright layer is the oxidized region by the plasma treatment.

The effect of N$_2$O plasma treatment on the water absorption of SiOF films and the origin of stabilization were studied. The N$_2$O plasma treatment effectively reduced the water absorption. It was found that the N$_2$O plasma treatment causes the oxidation of Si—F bond on the film surface and the oxidation reaction makes the surface dense silicon oxide. Thus, the oxidized surface inhibits the water absorption of films.

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