Effect of CH4 Plasma Treatment on O2 Plasma Ashed Organosilicate Low-k Dielectrics

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ABSTRACT

During an O₂ plasma ashing process, carbon depletion and subsequent moisture uptake caused an increase of kₐeff and the leakage current in an organosilicate (OSG) low-k dielectric. For dielectric restoration, an additional CH₄ plasma treatment on the O₂ plasma ashed OSG low-k dielectric was investigated using angle resolved x-ray photoelectron spectroscopy (ARXPS), XPS depth profiling, x-ray reflectivity (XRR), Fourier transform infrared spectroscopy (FTIR), Raman spectroscopy, and contact angle goniometer. After CH₄ plasma treatment on the O₂ plasma ashed OSG, the surface carbon concentration and surface hydrophobicity were partially recovered. A dense surface layer containing C=Ç bonds was found to have formed on the top of the damaged OSG. The C-V hysteresis and the leakage current were reduced as a result of the CH₄ plasma treatment. XPS depth profiling revealed that the recovery effect was limited to the surface region.

INTRODUCTION

Ultra low-k dielectrics with porosity are being developed to reduce the capacitance coupling in Cu interconnects for their lower polarizability and lower density of atoms and bonds [1, 2]. However, these porous low-k dielectrics tend to degrade during O₂ plasma ashing processes due to carbon depletion and moisture uptake. This dielectric loss may limit further scaling of low-k dielectrics. Mechanisms of plasma damage and recovery of the dielectric loss have generated enormous interests [3, 4]. Inspired by recent studies [5, 6] on the interaction between CH₄ plasma and pristine low-k dielectrics, this paper was focused on the recovery effect of CH₄ plasma treatment on O₂ plasma ashed organosilicate (OSG) low-k dielectrics. First, plasma damage in an O₂ plasma ashing process was evaluated. Then, CH₄ plasma treatment on O₂ plasma ashed OSG was studied by multiple analytical methods.

EXPERIMENT

The pristine OSG film in this study has a porosity of 25%, a density of 1.25 g/cm³, and a dielectric constant of 2.5. Samples were damaged by O₂ plasma for 5 seconds in March Asher under the condition of 300 W and 50 sccm. XPS depth profiling was performed in PHI 5700 x-ray photoelectron spectroscopy (XPS) system to investigate the change of atomic concentrations through OSG films. Nicolet Magna 560 FTIR was used to evaluate bonding configuration changes.
To study the recovery effect of CH$_4$ plasma treatment on O$_2$ plasma ashed OSG, samples were treated in an Oxford RIE chamber for 30 seconds under the condition of 50 W, 10 mtorr, and 30 sccm. The surface chemical composition was evaluated using XPS. The surface hydrophobicity was evaluated using CA100 Ramé-Hart Goniometer. The film density was measured using PANalytic’s X-ray Reflectivity machine. In addition to FTIR, RENISHAW Raman Spectroscopy with 514 nm laser wavelength was used to study carbon bonding configuration changes since FTIR was not sensitive to C=C sp$^2$ bonding configuration. Standard MIS capacitors were formed to measure C-V and I-V properties.

**RESULTS and DISCUSSION**

**Study of O$_2$ plasma damage**

To demonstrate the damage induced by O$_2$ plasma in OSG low k dielectrics, a very aggressive ashing recipe (300W, 50 sccm, and 5s) was intentionally used to severely damage a 90 nm thick OSG sample. The XPS depth profiling of the damaged OSG (Fig. 1) indicated that carbon depletion occurred not only near the surface but also deep into the bulk of the film. The whole film was almost converted to porous silica as a result of the severe plasma damage.

FTIR spectra of the pristine OSG and the O$_2$ plasma ashed OSG were compared in Fig.2. After O$_2$ plasma ashing, Si-CH$_3$ bonding configuration (~1274 cm$^{-1}$) disappeared and Si-OH and physisorbed H$_2$O bonding configurations (3100 cm$^{-1}$ ~ 3700 cm$^{-1}$) increased [7]. The high bond polarizability of Si–OH and the subsequently physisorbed H$_2$O (k > 70) were believed to cause higher $k_{eff}$ and leakage current.

**CH$_4$ plasma recovery effect**

In order to recover the dielectric loss caused by the O$_2$ plasma ashing process, additional CH$_4$ plasma treatment was performed on the O$_2$ plasma ashed OSG samples. Ionic and radical CH$_x$ group may interact with Si-OH to transform Si-OH into Si-CH$_3$.

In Fig. 3-1, XPS C 1s spectra for pristine OSG (a), O$_2$ plasma ashed OSG (b), and CH$_4$ plasma treated O$_2$ plasma ashed OSG (c) were presented. After O$_2$ plasma ashing process, the surface carbon concentration was almost completely removed. After CH$_4$ plasma was applied to the O$_2$ plasma ashed OSG, the surface carbon concentration was restored to a value more than...
that of pristine OSG. Fitted with the Gaussian and Lorentz function, the XPS C 1s peak after CH$_4$ plasma treatment could be deconvoluted into C=C (283.9 eV) and Si-CH$_3$ or C-C (285.1 eV) [8, 9]. Because the XPS peak for C-C bonding configuration overlapped with Si-CH$_3$, it was hard to differentiate them from each other. In Fig. 3-2, ARXPS peak area ratio for pristine OSG, O$_2$ plasma ashed OSG, and CH$_4$ plasma treated O$_2$ plasma ashed OSG were presented. In ARXPS, smaller detection angle (30°) provided more information about surface than bigger detection angle (90°). It was shown that there was more C=C bonding configuration on the surface than inside the bulk. This suggested one possible reaction mechanism – at the initial stage of CH$_4$ plasma treatment, energetic CH$_x$ radical species and ionic species reacted with Si-OH and formed an intermediate layer with Si-CH$_3$ bond; then, the further CH$_4$ plasma treatment caused the reaction between CH$_x$ and CH$_x$ to form C-C and C=C bonds at the topmost layer.

Figure 3. (1) XPS C 1s spectra and (2) ARXPS peak area ratio for pristine OSG (a), O$_2$ plasma ashed OSG (b), and CH$_4$ plasma treated O$_2$ plasma ashed OSG (c)

As shown by the water contact angle measurement results in Tab. 1, after O$_2$ plasma ashing process, the water contact angle decreased from 78.9° to 13.1°, indicating the surface became hydrophilic. This observation was consistent with the observed methyl loss and silanol increase in the XPS and FTIR spectra. After additional CH$_4$ plasma treatment, the surface hydrophobicity was partially recovered, as indicated by the increase of water contact angle from 13.1° to 71.7°.

Table 1. Contact angle measurements for pristine OSG, O$_2$ plasma ashed OSG, and CH$_4$ plasma treated O$_2$ plasma ashed OSG

<table>
<thead>
<tr>
<th>Sample</th>
<th>Water Contact Angle (°)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pristine OSG</td>
<td>78.9</td>
</tr>
<tr>
<td>O$_2$ plasma ashed OSG</td>
<td>13.1</td>
</tr>
<tr>
<td>O$_2$ plasma ashed =&gt; CH$_4$ plasma treated OSG</td>
<td>71.7</td>
</tr>
</tbody>
</table>

The XPS depth profiling result for CH$_4$ plasma treatment applied to O$_2$ plasma ashed OSG in Fig. 4 indicated that the carbon concentration recovery effect was limited to the top surface about 10 nm. There were two possible reasons. First, plasma CH$_4$ interaction with the surface was a self-limiting chemical reaction. Second, the densified surface and small pores due
to our aggressive O₂ plasma ashing recipe affected the penetration depth of CHₓ and H plasma species.

Figure 4. XPS depth profiling result for CH₄ plasma applied to O₂ plasma ashed OSG

Not much difference was observed for FTIR spectra of prior and after CH₄ plasma treatment because the recovery effect was limited to surface. As shown in the Raman spectra (Fig. 5), it was clear that after CH₄ plasma treatment, there were a certain number of C=C sp² bonds (~1600 cm⁻¹) on the surface [10]. Raman was not sensitive to carbon sp³ bonding due to its small scattering cross section.

Figure 5. Raman spectra for O₂ plasma ashed OSG and CH₄ plasma treated O₂ plasma ashed OSG

XRR simulation in Fig. 6 confirmed that a gradient surface layer was formed on the top of OSG. This was possibly due to the C=C, C-C, and CHₓ (x=1 or 2) bonding configurations. This densified layer might be useful for the pore sealing purpose which is under investigation now.
In Fig. 7, the C-V hysteresis was reduced after CH$_4$ plasma treatment, implying the partial removal of Si dangling bond and polar silanol group. In the I-V diagram, there was more reduction for leakage current in the small electric field range due to the removal of Si dangling bond and polar silanol group at the surface; there was less leakage current reduction in the big electric field range because of the charge buildup around defects inside the bulk of dielectric caused by aggressive O$_2$ plasma ashing recipe. Additionally, not much reduction of the dielectric constant was observed. This was understandable because the carbon rich surface layer only accounted for about 5% of the total sample thickness. Our C-V measurements could not resolve the difference with enough confidence.

**CONCLUSIONS**

During an O$_2$ plasma ashing process, replacement of Si-CH$_3$ by Si-OH caused moisture uptake, deterioration of the dielectric constant, and increase of leakage current. CH$_4$ plasma treatment on O$_2$ plasma ashed OSG was effective in partially restoring low k properties.
After CH₄ plasma treatment on O₂ plasma ashed OSG, a gradient densified layer was formed; surface carbon concentration and surface hydrophobicity were partially recovered. XPS carbon peak deconvolution and Raman spectra revealed the formation of C=C and Si-CH₃ or C-C on the top of OSG. The reduction of the C-V hysteresis and the leakage current indicated that Si-OH bonds and Si dangling bonds were partially removed by CH₄ plasma treatment. XPS depth profiling showed that the CH₄ plasma recovery effect was limited to the surface. This implied that in order to achieve full dielectric recovery, process optimization should include the restriction of O₂ plasma damage to low k dielectric surface and more effective plasma CH₄ interaction with Si-OH.

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REFERENCES