In situ fluorine-modified organosilicate glass prepared by plasma enhanced chemical vapor deposition

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In situ fluorine-modified organosilicate glass (FOSG) thin films and OSG thin films were deposited at various temperatures (250–400 °C) by the plasma enhanced chemical vapor deposition method. The fluorine content in the FOSG films was adjusted by varying the SiF\(_4\)/trimethylsilane gas flow ratio from 0.5 to 2. Film characteristics were investigated by examining the bonding configuration, index of refraction, surface composition, hardness, leakage current density, and breakdown field strength. The absorbance spectrum of Fourier transform infrared spectroscopy shows that the frequency of the Si–O stretching vibration mode in the FOSG films is shifted to a higher wave number (blueshift) with the increase of fluorine incorporation, while that at higher temperatures is shifted to a lower wave number (redshift). Meanwhile, the refractive index increases and decreases slightly with increasing fluorine content and deposition temperature, respectively. The dielectric constant of the FOSG is slightly lower than that of the OSG films. The FOSG films with higher fluorine content also exhibit higher mechanical hardness and higher dielectric breakdown voltage.

The higher mechanical strength of the FOSG films relative to that of the OSG films is as a consequence of the structural change accompanied by the incorporation of fluorine. © 2003 American Institute of Physics. [DOI: 10.1063/1.1578171]

I. INTRODUCTION

To mitigate the signal propagation delay, cross talk, and dynamic power consumption due to resistance and parasitic capacitance (RC), copper and low dielectric constant (low-k) materials as interconnect and inter-metal-dielectric (IMD) layers have replaced aluminum and SiO\(_2\), respectively, to improve the performance of decreasing device sizes. Nevertheless, despite the prevalence of copper interconnects in today’s advanced semiconductor devices, the implementation of lower-k materials has been much less successful and the SIA roadmap for the use of low-k IMD has been revised continuously since 1997.\(^1\) Therefore ongoing effort has been invested to develop reliable lower-k materials. One of the major candidates among many is the material comprised mainly of Si, C, O, H, and/or F prepared by the plasma enhanced chemical vapor deposition (PECVD) method, including F-doped oxide, or fluorinated silicate glass (FSG, Si\(_2\)OF\(_x\)), and C-doped oxides, or organosilicate glass (OSG, SiCO:H).\(^2\) The former, FSG (\(k = 3.4–3.7\)), with a slightly lower dielectric constant than conventional undoped silicate glass (USG, \(k = 3.9–4.1\)),\(^3–5\) has demonstrated its benefits as a feasible low-k material\(^6–10\) into IMD applications with suitable fluorine concentration (<5%).\(^11,12\) The latter, OSG film, has become one of major candidates for potential applications in a 130 nm device node because of its even lower dielectric constant (3.0 even down to 2.1).\(^13,14\) However, from a process integration point of view, this new group of low-k material, which usually has low density and high porosity, has yet to demonstrate improved mechanical properties, such as higher hardness and higher elastic modulus in the presence of the mechanical stress imposed by the chemical-mechanical polishing (CMP) process. In addition, it needs to have high resistance to stress migration and dry etching, without raising the dielectric constant.

In this article, we proposed an in situ fluorine-modified OSG (FOSG) thin film process to achieve superior mechanical properties while maintaining its low dielectric constant. Trimethylsilane (3MS), H–Si–(CH\(_3\))\(_3\), and/or tetrafluorosilane (SiF\(_4\)) are used as precursors for these plasma-enhanced chemical vapor deposited (PECVD) thin films. The thin films were deposited at various temperatures and fluorine content, and the optical refractive index, bonding configuration, mechanical properties, and electrical strength of these films were investigated in this study. The structural alteration mechanism that leads to improved mechanical properties and low dielectric constant are proposed and discussed.
II. EXPERIMENT

All thin film deposition was performed with an Applied Materials CETURA system in a 200 mm DxZ chamber. Fluorine-modified organic-silicon-glass (FOSG) composite films were prepared on p-type (100) silicon substrates by radio frequency (13.56 MHz) PECVD with trimethylsilane (3MS, Dow Corning® Z3MS™ CVD precursor) carried in vapor phase by inert helium gas to the reaction chamber. The 3MS precursor gas is mixed with oxygen (O₂) in the first deposition process step and tetrafluorosilane (SiF₄) is then introduced in situ into the reaction chamber and reacts with the 3MS–O₂ gas mixtures for the remainder of the deposition process. As a comparison, OSG films were deposited by removing SiF₄ from the reagent gas mixtures. The chamber pressure and rf power were maintained at 4 Torr and 600 W, respectively, throughout the deposition process. The deposition temperature and SiF₄/3MS flow ratio referred to as F ratio hereafter were varied between 250 and 400 °C, and 0–2, respectively. (Herein FSO: F ratio = 0; FSO-1: F ratio = 0.5; FSO-2: F ratio = 1; FSO-3: F ratio = 1.5; and FSO-4: F ratio = 2.)

The as-deposited films were analyzed for thickness and refractive index (RI, at 633 nm) by a reflectometer and/or ellipsometer using a Nano-Spec® 9100. Fourier transform infrared spectroscopy (FTIR), where the spectrum were taken with the background subtracted by a standard bare silicon wafer, was operated in the absorbance mode with a BioRad Win-IR PRO, in order to examine Si–F, Si–CH₃, and Si–O bonding configurations in the FOSG and OSG films. Film composition was determined by x-ray photoelectron spectroscopy (XPS) and Rutherford backscattering spectroscopy (RBS). A MTS Nano Indentor XP system was used to measure nano-hardness and modulus of these films. The sample thickness for the nano-hardness measurement was approximately 1 μm and the depth penetration was about 100 nm at ~0.3 mN down force. Each hardness entry is the average over five measurements. For electrical characterization, a mercury probe was employed to measure the dielectric constant, leakage current density, and breakdown field strength of the FOSG films at 1 MHz.

III. RESULTS AND DISCUSSION

With a constant deposition time, the variations of the growth rate and refractive index (RI) of the FOSG films deposited at various temperatures and F ratios are shown in Figs. 1 and 2, respectively. Apparently, the growth rate of the FOSG does not vary over the F ratio (0–2) but decreases with increasing deposition temperature. The monotonic decrease in the growth rate with temperature is almost the same for the films with various F ratios, indicating that the films with different F ratio follow a similar kinetics. The refractive index of the FOSG films averaged over nine measured points per wafer exhibits a slightly increasing trend with the F ratio regardless of deposition temperature, and has a decreasing trend with increasing deposition temperature from 250 to 350 °C at all F ratios (Fig. 2). The results suggest that the properties of the as-deposited films, such as composition, density, and bonding configuration, may have been changed appreciably by varying the deposition temperatures and/or the addition of fluorine. Also, the deposition temperature seems to dominate over the F ratio in affecting film properties.
To further investigate the causes of the variations in the growth rate and refractive index, the bonding states of the FOSG composite films were analyzed by IR absorption spectra over the range of 400–4000 cm\(^{-1}\). Figure 3 shows the FTIR spectra from a series of the FOSG films of 1 mm thickness deposited at 400 °C. The spectra exhibit the absorption peaks at 440, 802, 810, 900, 1060, and 1270 cm\(^{-1}\) corresponding to Si–O rocking, Si–CH\(_3\) bending, Si–O bending, Si–F\(_x\) stretching, Si–O stretching, and Si–CH\(_3\) stretching, respectively, and bands ranging from 2100 to 2235 and 2855 to 2960 cm\(^{-1}\) corresponding to SiH\(_x\) and CH\(_x\), respectively.

Note that the absorption peak at 900 cm\(^{-1}\) is comprised of Si–F\(_x\) stretching and Si–CH\(_3\) wagging modes, where only SiCH\(_3\) exists in the OSG while two modes coexist in the FOSG.

It is apparent from Fig. 3 that the Si–F\(_x\) stretching mode increases as the F ratio (fluorine content) in the FOSG films increases; meanwhile the peak intensities of both the CH\(_x\) group (around 1270 and 2900 cm\(^{-1}\)) and the Si–H\(_x\) group (around 2200 cm\(^{-1}\)) decrease with increasing F ratio. The above observations suggest that the increase in fluorine content in the FOSG films is accompanied by a reduction in carbon and hydrogen content, which agrees with the results from elemental analysis (by XPS and RBS) shown in Table I.

As the F ratio increases during the deposition process, more Si atoms are terminated with –F, instead of –CH\(_3\) and –H, groups in the network. Based on the information gathered from Fig. 3, the chemical reactions responsible for the formation of the OSG and FOSG films are proposed in Figs. 4 and 5, where \(\Theta_C\) and \(\Theta_F\) are the Si–O–Si bond angles in the OSG and FOSG films, respectively.

It is presumed that the OSG is an \(a\)-SiOC:H film compound with a lot of open volume and “imperfect” Si–O–Si \(sp^3\) tetrahedra terminated by CH\(_3\) and/or H, plus some loose, unsaturated methyl groups (CH\(_3\)) trapped in the open cores of the structure. As a consequence, the long-range order of the Si–O–Si tetrahedra network (as that in a perfect SiO\(_2\)) is deteriorated by the presence of these Si–H and Si–CH\(_3\) bonds so that the structure is more open (more free volume). This is even more so in the presence of the loose CH\(_3\) methyl groups, which exist as the free radicals in the \(a\)-SiOC:H structure. When SiF\(_4\) is introduced into the deposition chemistry, Si–F bonds come into formation, in consumption of the Si–O–Si bonds. In this scenario, the Si–O–Si bond network is terminated with the highly electronegative F ions instead of –CH\(_3\) or –H so that the Si–O–Si bond angle becomes larger and the network becomes less polarizable, which agrees with the mechanism proposed by Kim \textit{et al.}\(^{15}\) Therefore the Si–O–Si bond angle (\(\Theta_F\)) in the FOSG films is larger than that (\(\Theta_C\)) in the OSG films as shown in Figs. 4 and 5. In addition, the preferential formation of the Si–F bonds suppresses the formation of the Si–H, more bulky Si–CH\(_3\) bonds, and free CH\(_3\) groups. As a result, the structures of the FOSG films are less open with the higher packing density, compared with those of the OSG films. Also, from the aforementioned results and discussions, the slight increase in the refractive index of the FOSG films with in-

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**Table I. Film composition of FOSG (F ratio=1) and OSG (F ratio=0).**

<table>
<thead>
<tr>
<th></th>
<th>FSO-1</th>
<th>FSO</th>
</tr>
</thead>
<tbody>
<tr>
<td>%Si</td>
<td>35.2</td>
<td>36±3</td>
</tr>
<tr>
<td>%O</td>
<td>40.4</td>
<td>41±3</td>
</tr>
<tr>
<td>%C</td>
<td>20.1</td>
<td>23±3</td>
</tr>
<tr>
<td>%H</td>
<td>N/A</td>
<td>N/A</td>
</tr>
<tr>
<td>%F</td>
<td>4.0</td>
<td>N/D</td>
</tr>
</tbody>
</table>

Note: N/A=not analyzed, N/D=not detected. The atomic percents are normalized to 100%.

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**Figure 4.** Proposed chemical reaction responsible for OSG formation.

**Figure 3.** Typical FTIR spectra from FOSG films with various F ratios deposited at 400 °C.
creasing $F$ ratio in Fig. 2 is likely indicative of the lower porosity and fluorine incorporation.

Effects of process parameters on the peak position of the Si–O–Si stretching mode in the films are shown in Fig. 6. It can be seen that the peak position of the Si–O–Si stretching mode is shifted to higher wave number (blueshift) with increasing $F$ ratio, and to lower wave number (redshift) with decreasing deposition temperature. This is due to the high electron affinity and electronegativity of fluorine,\textsuperscript{15} which attracts more electrons closer to the $F^-$ ions and depletes the electrons in the neighboring Si–O bonds. As a consequence, the Si–O–Si bonds are weakened so that they become less rigid and “more stretchable,” resulting in a higher stretching frequency from FSO to FSO-4, as shown in Figs. 3 and 6. Also observed in Fig. 6, the effects of the deposition temperature actually compete against those of fluorine incorporation. In this case, the higher deposition temperatures lower the frequency of the stretching Si–O–Si bonds in the structure of the FOSG films. This implies that electronic defects are annihilated and bond angles are adjusted at high deposition temperatures so that the Si–O–Si bond strength is restored to a certain degree, in the presence of fluorine in the structures.

A closer inspection of Fig. 3 also reveals that the Si–O–Si stretching peak is actually divided into two peaks, the main peak at around 1050 cm\(^{-1}\) and the shoulder peak at around 1150 cm\(^{-1}\). No matter whether fluorine is incorporated into the FOSG films or not, the shoulder peak remains behind the main Si–O–Si peak, although it becomes increasingly difficult to differentiate between the two peaks at higher $F$ ratios, due to the blueshift and hence the overlap of the shoulder peak with the main peak. Pai \textit{et al.}\textsuperscript{16} suggested that the shoulder peak is due to the in-phase and out-of-phase movements of the Si–O–Si bond; Chou \textit{et al.}\textsuperscript{17} and Grill \textit{et al.}\textsuperscript{18} proposed that the shoulder peak is related to the porosity of an oxide with caged Si–O bonds and reflection of enhanced porosity in the films; Lee and Park\textsuperscript{19} thought that the addition of fluorine results in microvoids that account for the appearance of the shoulder peak. In the current study, this split in the stretching peak is definitely more related to the film microstructure than F incorporation, which affects the strength of the Si–O–Si bonds, as evident from the peak shift in Fig. 6.

Figure 7 shows the relative fluorine and carbon content of the FOSG films as a function of the deposition temperature. The relative bond concentrations of fluorine and carbon incorporated in the FOSG composite films are calculated by the following equation normalized to the peak height of the Si–O–Si stretch mode:

$$\text{Relative} \{F\} \text{ or } \text{Relative} \{C\} \text{ content} (%) = \left\{ \frac{I_F \text{ or } I_C}{I_F \text{ or } I_C + I_{\text{Si-O}}} \right\} \times 100\%,$$

where $I_{\text{Si-O}}$, $I_C$, and $I_F$ are the peak heights of the stretching vibration modes of the Si–O–Si at 1060 cm\(^{-1}\), Si–CH\(_3\) at 1270 cm\(^{-1}\), and Si–F\(_x\) at around 900 cm\(^{-1}\), respectively. Both carbon and fluorine contents decrease with increasing the deposition temperature. The increasing ratio of the Si–O–Si bonds suggests the abundance of the Si–O–Si bonds at higher temperatures. This helps the FOSG films restore part

FIG. 5. Proposed chemical reaction responsible for FOSG formation.

FIG. 6. Peak locations of the wave number of Si–O–Si stretching mode as a function of $F$ ratio (deposited at 350 °C typically) and deposition temperature.

FIG. 7. Relative fluorine and carbon content incorporated in FSO-4 films as a function of deposition temperature.
of the bond integrity and tetrahedral structure of a perfect SiO$_2$, leading to the improved mechanical properties as shown below.

Mechanical hardness and modulus of elasticity of the resulting OSG and FOSG films are plotted as a function of $F$ ratio in Fig. 8. The figure clearly exhibits a trend of improvement in hardness and modulus as the $F$ ratio increases, which can be attributed to the higher packing density of the films due to the less loose CH$_x$ methyl groups by fluorine incorporation, as discussed previously. Meanwhile, it is noted that the hardness (2 to 3 GPa) of the FOSG films at 400 °C is higher than that of the OSG (~1.5 GPa) films with more free volume. That makes the FOSG a potential (and better) substitute for the OSG to be implemented as an IMD film in the integration scheme.

Figure 9 shows the permittivity (dielectric constant) of the thin films measured at 1 MHz. Apparently, the dielectric constant decreases slightly as the $F$ ratio increases in general, and the films deposited at the lower temperatures exhibit the lower values. Lim et al.$^{20}$ proposed that fluorine attracts and replaces relatively more polarizable constituents, which leads subsequently to the lower dielectric constant. Shapiro et al.$^{21}$ suggest that replacing the Si–O in the SiO$_2$ matrix with the Si–F reduces the electronic polarizability of the matrix and thus the electronic contribution to the dielectric constant. From Fig. 9, the lowering of the dielectric constant in the FOSG films with increasing $F$ ratio is due to the polarizability of the (SiO$_3$F) tetrahedral structure, which has been described in Fig. 5, despite the higher packing density in these films. In this case, ionization polarization, instead of electronic polarization, seems to play a dominant role in the reduction of permittivity in the FOSG, since the refractive index actually increases with $F$ ratio as shown in Fig. 2.

Figure 10 shows the dependence of the leakage current on the electric field from the FOSG ($J$-$E$ plot) films of various $F$ ratios and deposition temperatures, relative to that from a typical OSG film. The leakage current increases with the electric field, and two plateaus can be clearly identified in the fluorine-incorporated films. On the other hand, the $J$-$E$ plot of the FSO (OSG) film does not exhibit a plateau in its $J$-$E$ plot, opposed to all the others in Fig. 10. Supposedly, this is the result of two forms of the bonding configuration existing in the FOSG films. The higher plateau is associated with the fluorine-incorporated structure while the lower one related to the relatively fluorine-free structure. In addition, there is a strong temperature effect on the breakdown field of the FSO-4. This can also be attributed to the changes in the bonding configuration at various temperatures. As shown in Figs. 6 and 7, the lower temperature results in the more stretchable Si–O–Si bonds, more CH$_x$ groups, and more free volume present in the films. Therefore the breakdown field strength decreases at the lower temperatures. The breakdown field of the investigated FOSG films deposited at high temperatures is in the range of 6.5–8.5 MV/cm, which is higher than that of the fluorine-free OSG film. This result suggests that the modified FOSG films are excellent candidates for the IMD layers in the ultralarge scale integration circuit applications.

IV. CONCLUSION

The composition, bonding configuration, optical, mechanical, and electrical properties of in situ fluorine-modified OSG (FOSG) films using trimethylsilane (3MS), tetrafluoro-
rosilane (SiF₄), and oxygen (O₂) as precursors by the PECVD method have been investigated. The refractive index of the FOSG decreases with increasing deposition temperature yet increases with increasing fluorine content in the films. Higher fluorine content in the FOSG films also accounted for the improved mechanical hardness and modulus, and the lower dielectric constant. Compared with the OSG films, the FOSG films exhibit a bimodal behavior in the dielectric breakdown and the higher deposition temperatures improve their breakdown field strength. These results can be accounted for by the changes in composition and bonding configuration, as determined from FTIR and elemental analyses. Relatively speaking, the modified FOSG appears to be a more promising low dielectric constant material for IMD application than the OSG.

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