Integration Damage in Organosilicate Glass Films

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Abstract

This study compares integration damage (ID) to two non-mesoporous organosilicate glass (OSG) films and several mesoporous OSG films with completely connected pores. The results show that the mesoporous OSG films are more susceptible to integration damage than are the non-mesoporous films.

Introduction

Low dielectric constant (low-κ) interlayer dielectric (ILD) materials are necessary to mitigate RC propagation delay and reduce power consumption and crosstalk in advanced interconnects.(1) Lowering the κ-value of a material requires either altering the chemical bonding to reduce the bond polarizability or decreasing the number of bonds (density) in a material.(2) Most dielectric materials will require a density decrease by increasing the free volume (micropores < 2nm in diameter) or mesoporosity (2 - 50 nm diameter pores) to achieve κ<2.2. Unfortunately, lowering the density also compromises the mechanical strength and other properties of the material.(2)

Low density, connected mesopores, and low mechanical strength create a host of integration problems including integration damage to the film.(3-4) OSG films contain Si-R groups, where R is an organic moiety such as a -CH3 group. The Si-R groups make OSG films hydrophobic and lower the density by breaking up the tetrahedral Si-O bonding. However, the carbon component is susceptible to degradation when exposed to the reactive plasmas used for capping, etching, and ashing processes; especially oxidizing plasmas. Plasmas can induce chemical modifications in the film and cause film densification, dangling bonds and defects, and moisture uptake.(5) All of these can increase the κ-value or cause other integration problems.

Results and Discussion

Recently International SEMATECH (ISMT) monitored several OSG films for change in κ caused by ID while integrating the films into their Cu/Damascene test chip and using their standard processing flow, Table 1. Several mesoporous OSG films with connected pores exhibited a large increase in κ due to ID. In contrast, non-mesoporous OSG films showed much smaller changes in κ. Thus, connected mesoporosity or low density appear to facilitate film damage to OSG films during processing by allowing reactive species to more easily penetrate the film. However, process optimization at ISMT has alleviated this problem for some mesoporous OSG films.

Various plasma pretreatments (PPT) have been reported to form densified and chemically modified interface layers on OSG films, and these skin layers can prevent film damage by photoresist ash processes.(6-9) This study reports the effects of oxygen plasma ashing and a nitrogen-based plasma pretreatment on several mesoporous and two non-mesoporous blanket films.

OSGs-1, 4, 5, and 6 are spin-on mesoporous OSG films. OSG-2 is the non-mesoporous version of OSG-1 that was deposited using the same precursor without the porogen. All of the SOD mesoporous films were proprietary methylsilsesquioxane-like materials provided by different suppliers. OSG-3 is a trimethylsilane-based, PECVD OSG film that also incorporates Si-CH3 groups. Table 2 lists the films’ properties. The PPTs were conducted in a commercial PECVD tool at 350°C (setpoint). A Gasonics (IPC L3500) asher was used for the oxygen plasma ashing.

The XSEM images in Figure 1 show that the PPT causes a thin (<100Å) skin layer to form on the non-mesoporous OSG-2 that protects it from subsequent ash damage. Ashing OSG-2 without a PPT caused a very thick densification layer. Non-mesoporous OSG-3 exhibited nearly identical behavior. The PPT modified layer in OSGs-2 and 3 is limited to the surface for the exposure times used because its growth rate is slow. In contrast to the non-mesoporous OSG films where the skin layer remains very thin at the film surface, XSEM images of OSG-1 after PPTs for 30s and 60s, Figure 2, show a densification layer that grows thicker with PPT time. Thus it grows more rapidly in the mesoporous film.

TOF-SIMS depth-profiled chemical analysis, Figure 3, determined that the densification layer is nitridated and carbon depleted by the PPT consistent with previous findings on similar OSG films.(7,9) Some fluorination was also observed due to residual fluorine in the plasma chamber. The nitridated layer also grew deeper with increasing PPT time in the mesoporous films whereas it formed only a thin skin layer in the non-mesoporous films.
SIMS indicates that ashing only caused densification without nitridation (not shown) for all films.

Figures 4-5 show how $\kappa$ and Si-CH$_3$ absorptions change after a 60s PPT, 60s PPT + 10s O$_2$ plasma ashing, and after ashing without a PPT. The aforementioned properties are relatively constant for the non-mesoporous OSG films after both the 60s PPT and 60s PPT + ash. However, without the PPT, ashing causes substantial changes in these properties. Thus, the 60s PPT effectively protects OSG-2 and OSG-3 from ash damage by forming a protective, skin layer.

In contrast to the non-mesoporous films, the 60s PPT does not protect the mesoporous OSG films from ash damage, and the PPT alone causes large changes in the films’ properties. The thickness decreases and RI increases, the $\kappa$-value increases, and the Si-CH$_3$ peaks completely disappear. Silanol and water absorptions increase in the FTIR as the Si-CH$_3$ and Si-C peaks decrease.

These results demonstrate that the mesoporous films are more susceptible to ID than are the non-mesoporous OSG films. In the cases of OSG-2 and OSG-3, the PPT forms a skin layer that effectively barriers the rest of the film from damage during ashing, at least for the plasma exposure times used in this study. A skin layer also forms on the surface of OSGs-1,4,5 and 6, but this layer grows rapidly and does not seal off these films from the reactive species in the PPT or ash plasmas. Although only two plasmas (oxygen and nitrogen-based) were used in this study the data suggest that the mesopores are more difficult to close off at the surface of the film, and the connected pore structure allows reactive species to more rapidly penetrate the film beyond the densified interface layer. However, lower density alone could be responsible for the faster diffusion rate.

Positronium annihilation lifetime spectroscopy (PALS) (10) indicates that the modified layer caused by the PPTs does close off the mesopores. Positronium that is implanted into the mesoporous OSG-1 can diffuse out of the as-deposited film. However, after the PPT, the resulting skin layer prevents positronium escape from the film. Thus, the actual diffusion mechanism of reactive species from the N-based and O-based plasmas is unclear. Two possibilities are rapid diffusion through the low-density matrix material even if the pores are collapsed or pore clogging due to chemical modification that blocks positronium but allows other species to diffuse. What is clear is that the mesoporous OSG films used in this study were much more susceptible to ID than non-mesoporous OSG films.

Films with isolated pores may be less susceptible to ID, but a closed pore OSG film was not available for this study. We are now exploring other plasma chemistries to determine if they are more benign to mesoporous OSG films, and we are using PALS to explore the diffusion mechanism and how pore size and structure affect it.

Conclusions

Our study shows that several mesoporous OSG films are more susceptible to ID than two non-mesoporous OSG films. A nitrogen-based plasma forms a dense, nitridated skin layer on the non-mesoporous OSG films that protects them from subsequent plasma damage. The skin layer was not confined to the surface of the mesoporous OSG films and grew deeper into these films with exposure time. The results suggest that connected pores and/or low density facilitate the diffusion of damaging, reactive species into mesoporous OSG films, and rigorous process optimization is necessary to successfully integrate these films.

Acknowledgements

We gratefully acknowledge the staff at Motorola's Dan Noble Center.

References

11. Data provided by the material supplier.

Table 1. SEMATECH data for several OSG low $k$ films that were integrated into their standard test chip. The as-deposited $\kappa$-value increases by $\Delta \kappa$ after integration due to ID. The $\kappa$ after integration was extracted from capacitance measurements on interdigitated comb/serpentine structures using RAPHAEL™ simulation software.

<table>
<thead>
<tr>
<th>Material</th>
<th>$\kappa$ after Integration</th>
<th>MOSCAP (blanket film)</th>
<th>$\Delta \kappa$</th>
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<tbody>
<tr>
<td>OSG-A</td>
<td>2.92 ± 0.11</td>
<td>2.92 ± 0.02</td>
<td>0</td>
</tr>
<tr>
<td>OSG-B</td>
<td>3.0 ± 0.30</td>
<td>3.07 ± 0.03</td>
<td>.07</td>
</tr>
<tr>
<td>OSG-C</td>
<td>2.75 ± 0.30</td>
<td>2.76 ± 0.03</td>
<td>.01</td>
</tr>
<tr>
<td>OSG-I</td>
<td>2.77 ± 0.12</td>
<td>2.2 ± 0.01</td>
<td>0.57</td>
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<tr>
<td>OSG-D</td>
<td>2.39 ± 0.10</td>
<td>2.09 ± 0.03</td>
<td>0.3</td>
</tr>
<tr>
<td>OSG-E</td>
<td>2.75 ± 0.30</td>
<td>2.12 ± 0.03</td>
<td>0.63</td>
</tr>
<tr>
<td>OSG-F</td>
<td>2.95 ± 0.30</td>
<td>2.29 ± 0.03</td>
<td>0.66</td>
</tr>
</tbody>
</table>

OSGs A, B, and C are non-mesoporous PECVD films.
OSGs I, D, E, and F are mesoporous spin-on films with connected pores.
Table 2. Material properties for the films used in this study (11, 12)

<table>
<thead>
<tr>
<th></th>
<th>OSG-1 (SOD)</th>
<th>OSG-2 (SOD)</th>
<th>OSG-3 (CVD)</th>
<th>OSG-4 (SOD)</th>
<th>OSG-5 (SOD)</th>
<th>OSG-6 (SOD)</th>
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<tr>
<td>Mesoporosity (%)</td>
<td>58</td>
<td>0</td>
<td>0</td>
<td>~50</td>
<td>~55-60</td>
<td>-</td>
</tr>
<tr>
<td>Avg. Pore Size (nm)</td>
<td>2.5</td>
<td>Microporous</td>
<td>Microporous</td>
<td>~2-3</td>
<td>2.5</td>
<td>2.6</td>
</tr>
<tr>
<td>Pore Structure</td>
<td>Connected</td>
<td>Closed (isolated)</td>
<td>Closed (isolated)</td>
<td>Connected</td>
<td>Connected</td>
<td>Connected (some isolated)</td>
</tr>
<tr>
<td>Density (g/cc)</td>
<td>0.89</td>
<td>-</td>
<td>1.4</td>
<td>-</td>
<td>0.94</td>
<td>.90</td>
</tr>
<tr>
<td>%C</td>
<td>~12</td>
<td>~12</td>
<td>~18</td>
<td>-</td>
<td>~6</td>
<td>-</td>
</tr>
</tbody>
</table>

Fig. 1. XSEM images of OSG-2, A) 60s PPT (N-based) only, and B) 10s O$_2$ plasma ash only. A 60s PPT + 10s O$_2$ plasma ashed sample looked identical to (A). An MBond layer was deposited on top of the film to facilitate sample preparation, and the samples were stained to decorate the damaged region.

Fig. 2. XSEM images of OSG-1, A) 30s PPT (N-based) only, and B) 60s PPT (N-based) only. OSGs-4, 5, and 6 behaved as OSG-1 above. An MBond layer was deposited on top of the film to facilitate sample preparation, and the samples were stained to decorate the damaged region.

Fig. 3. TOF-SIMS profiles on OSG-1. A) as deposited, and B) 60s PPT (N-based) only. OSGs-4, 5, and 6 showed similar behavior.

Fig. 4. Hg-probe MIS MOSCAP data showing $\kappa$ versus condition.

Fig. 5. The % loss of the Si-CH$_3$ peak (~1275 cm$^{-1}$) area versus process condition. The data is normalized for thickness variations. The -CH$_3$ peak at ~2970 cm$^{-1}$ shows a similar trend.