Effect of Porogen Residue on Chemical, Optical, and Mechanical Properties of CVD SiCOH Low-\(k\) Materials

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The effect of He/H\(_2\) downstream plasma on chemical vapor deposition -CVD- low-\(k\) films with different porosities was studied. The results show that this plasma does not reduce the concentration of Si–CH\(_3\) bonds in the low-\(k\) matrix and that the films remain hydrophobic. However, mass loss and reduction in bulk C concentration were observed. The latter phenomena are related to the removal of porogen residue formed during the UV curing of the low-\(k\) films. It is demonstrated that the porogen residue removal changes the films’ porosity and mechanical properties. The depth of the modification is limited by the penetration of H radicals into the porous low-\(k\) films.

The plasma-induced damage of porous SiCOH-type low-\(k\) materials is one of the key problems in Cu/low-\(k\) integration.\(^1\) The most severe plasma damage occurs during photomask -resist- removal.\(^2\) The reason for this phenomenon is the hybrid nature of the SiCOH materials. These materials contain a SiO\(_2\)-like matrix where part of the terminating oxygen atoms is replaced by organic groups -most often CH\(_3\)-. The organic groups provide the films’ hydrophobicity, which is important for the dielectric constant reduction. The hybrid nature is the reason for the different reactivities of the low-\(k\) components. For instance, the reactive species from plasma such as O radicals penetrate into the porous network of the low-\(k\) films and may result in substantial carbon depletion, thus leading to an in-crease in the \(k\) value. The depth of penetration is defined by the diffusion coefficient of active radicals into the pores and their re-combination probability on the pore wall.\(^3\)

Two commonly known approaches are used for the resist removal: –i– a low temperature, low pressure anisotropic plasma, where the photoresist is removed by an ion-assisted process, oxidizing or reducing plasma chemistries at low temperatures and –ii– hydrogen-based downstream plasma -DSP- where the resist is re-moved at high temperatures by a thermally activated chemical process. According to recent publications, the option with He:H\(_2\) and Ar:H\(_2\) DSPs prevents carbon depletion from the low-\(k\) materials matrix.\(^4,5\) Therefore, the degradation of the dielectric constant is minimal, and these processes are considered the most attractive options for the microelectronic industry.

The porosity in advanced chemical vapor deposition -CVD- low-\(k\) films is created after deposition by the removal of a sacrificial phase -porogen- by UV-assisted thermal curing. UV curing also results in formation of the Si–O–Si network with improved mechanical properties.\(^7,8\) The porogen molecules are normally cyclic hydrocarbons\(^9\) that are photodissociated by UV light with the formation of volatile hydrocarbons and nonvolatile carbon-rich residues.\(^10,11\) The effect of the porogen residues on the low-\(k\) properties and the plasma processing compatibility are largely unknown. Fourier transform infrared -FTIR- spectrometry has a limited sensitivity to amorphous carbon -C\(_x\)C- and C–C bonds-, and this is the reason why it is difficult to monitor porogen residues with this technique. Recent studies using Raman spectroscopy and UV spectroscopic ellipsometry -UVSE- allowed a quantitative evaluation of porogen residues.\(^10,11\)

In this article, using FTIR spectroscopy, time-of-flight secondary-ion mass spectroscopy -TOF-SIMS-, UVSE, and mass measurements, we demonstrate that the porogen residues react with hydrogen radicals and are removed during the processing in He:H\(_2\) DSP.\(^4\) The porogen residue removal has a significant impact on the chemical properties of low-\(k\) films. The main purpose of this work is the evaluation of the amount and properties of porogen residues formed in low-\(k\) films with different pore sizes and porosities and also of the effects of UV-curing conditions. For this reason we evaluated four different low-\(k\) materials.

**Experimental**

**Materials and experimental procedure.**— SiOCH low-\(k\) films of 180 and 500 nm with porosities in the range of 23–36% were de-posited on 300 mm Si wafers -Table I-. The \(k\) values were in the range of 2.2–2.5. The matrix material was codeposited with sacrificial porogen by plasma-enhanced chemical vapor deposition -PECVD-. Then, the films were UV cured at 430°C. A broad-band UV curing was performed for all films except Ea. The materials “B” were deposited with different porogen concentrations and different porosities, but they were cured using the same UV source. The materials “E” were deposited in the same conditions but were cured by two different UV sources. The He:H\(_2\) 20:1 -DSP- treatments of the blanket low-\(k\) films were performed in a 300 mm asher. The films were treated with He:H\(_2\) DSP at 280°C using 20–700 s.

**Instrumentation.**— The surface hydrophobic properties were evaluated using H\(_2\)O goniometry. The chemical composition and bonding structure were analyzed using a N\(_2\)-purged FTIR spectrometer Biorad Q5200 ME. The TOF-SIMS analysis was done using an IONTOF IV instrument in a noninterlaced dual-beam mode with a Xe sputtering beam \(-1\) keV, 80 nA, 500 ~500 ~m- and a bunched 15 keV Ga analysis beam ~100 ~100 ~m area- to detect secondary ions. The optical properties and the depth of the plasma modification were measured by a UVSE in the range of 150–895 nm by using an Aleris ellipsometer from KLA Tencor. The optical properties were determined by fitting models to the measured spectra of the ellipsometric polarization angles at 70° by single- and double-layer optical models using the Marquardt-Levenberg algorithm.\(^11,12\) For double-layer spectroscopic ellipsometry modeling, the bottom

<table>
<thead>
<tr>
<th>Film</th>
<th>Open porosity -%</th>
<th>Targeted (k) value</th>
<th>Thickness -nm</th>
<th>Young’s modulus -GPa</th>
<th>UV curing source wavelength -nm</th>
</tr>
</thead>
<tbody>
<tr>
<td>B2</td>
<td>23</td>
<td>2.5</td>
<td>180</td>
<td>7.43</td>
<td>~200 -broad band</td>
</tr>
<tr>
<td>B3</td>
<td>36</td>
<td>2.2</td>
<td>500</td>
<td>5.54</td>
<td>~200 -broad band</td>
</tr>
<tr>
<td>Ea</td>
<td>32</td>
<td>2.3</td>
<td>180</td>
<td>4.48</td>
<td>~172 -narrow band</td>
</tr>
<tr>
<td>Eb</td>
<td>34</td>
<td>2.3</td>
<td>180</td>
<td>3.8</td>
<td>~200 -broad band</td>
</tr>
</tbody>
</table>

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layer was assumed to have optical properties of the as-deposited film, while the optical characteristics of the top modified layer were determined by fitting. The mass change was measured by mass balance metrology – Mentor SF3 from Metryx – on 300 mm wafers ~0.04 mg accuracy~. The open porosity and pore-size distributions were evaluated using ellipsometric porosimetry –EP~. The mechanical properties, the elastic modulus –EM~, and the hardness of the low-k dielectric films were measured using a nanoindenter –NI~XP system –MTS Systems Corporation~ with a dynamic contact module and a continuous stiffness measurement option under the constant strain rate condition. A standard three-sided pyramid diamond indenter tip ~Berkovich~ was pressed into each sample; both the depth of penetration and the applied load were monitored.

**Results and Discussion**

**Change in composition.** – The changes in the IR absorbance of the low-k materials before and after exposure in He/H2 plasma are close to the measurement errors. Therefore, only the magnifications of the selected absorbance bands are shown. There is neither reduction in Si–CH3 concentration ~Fig. 1~ nor OH group incorporation ~Fig. 2~. This shows that the films remain hydrophobic. Only discrete changes are observed: the redshift in the Si–CH3 absorbance and a minimal H2O amplitude increase ~around 3200 cm⁻¹~ presumably due to an increase in the low-k pore radii after the He/H2 DSP plasma exposure. The observations are typical of all studied films. The FTIR results are supported by H2O-goniometry measure-

**Figure 1.** Color online. The chosen magnification of FTIR spectra reflecting the absorbance band of Si–CH3 groups ~1285–1260 cm⁻¹~ of as-deposited and He/H2 plasma treated Eb films.

**Figure 2.** Color online. The chosen magnification of FTIR spectra showing absorbance bands related to Si–OH, H2O groups ~3800 - 3000 cm⁻¹~, and C–H and C\v C sp² groups ~1700–1450 cm⁻¹~.

**Figure 3.** Color online. C-depth profile for as-deposited and He/H2 treated EB films as measured by TOF-SIMS. The embedded graph presents the sputtering time proportional to depth of modification ~C depletion~ vs He/H2 exposure time.

ments showing that surface contact angles with H2O remain higher than 80° for all the studied low-k films. Therefore, both the surface and the bulk of the low-k films remained hydrophobic, and one can conclude that no plasma damage in the low-k matrix has occurred.

Figure 2 shows a magnification of the FTIR spectra in the 1450–1700 cm⁻¹ range that indicates a reduction in the 1600 cm⁻¹ absorbance band related to the C\v C sp² bond with the time of the He/H2 plasma treatment and some changes in C–H groups ~1475–1550 cm⁻¹~. The presence of the C\v C and C–H groups is described as the signature of porogen residues. A reduction in the absorbance bands of C\v C and C–H groups might indicate a removal of the porogen residues after the He/H2 plasma exposure ~Fig. 2b~. However, the C\v C and C–H group amplitudes were very small, and it agrees with the literature.

TOF-SIMS analysis ~Fig. 3~ shows a reduction in the carbon concentration as a result of the He/H2 plasma exposure. The depth of carbon depletion depends on the exposure time ~zoomed area in Fig. 3~. The sputtering time in TOF-SIMS in first approximation is proportional to the film thickness. Therefore, the depth of carbon depletion has a tendency to saturate with time, which allows us to assume that this process is limited by the diffusion of H radicals from the He/H2 DSP plasma. The penetration depth of the H radicals must be determined by the properties of low-k films such as pore size, open porosity, porogen content, and the recombination coefficient of H radicals on the pore walls.

The reduction in carbon concentration is limited: The carbon concentration in the top part of the films stays the same after 35, 140, and 700 s ~Fig. 3~. Therefore, this carbon depletion process is limited by the porogen residue content in the film matrix. The change in carbon concentration is in qualitative agreement with the mass measurements ~Fig. 4~. The mass of low-k films is reduced as a result of the exposure to the plasma and also has a tendency to saturate at sufficiently long exposure time. This agrees with TOF-SIMS results and suggests that the depletion of carbon concentration in TOF-SIMS and mass loss have the same nature.

The phenomena observed in TOF-SIMS and mass balance measurements have a seeming contradiction with the FTIR results ~no Si–CH3 group depletion~. Therefore, TOF-SIMS and mass balance reflect the concentration change of the carbon compounds, whose bonding structure is almost invisible in the FTIR spectra. FTIR has a limited sensitivity to an amorphous carbonlike porogen residue ~Fig. 2~. Therefore, the most reasonable assumption is that the carbon depletion and mass loss are related to the removal of the porogen residue.

To prove this assumption, we studied the plasma exposed samples by UVSE. The spectra of as-deposited ~solid lines~ and 700
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Figure 4. -Color online- Mass loss after He:H2 plasma modification as measured by mass balance on 300 mm wafers. The numbers show percentage mass loss in modified layers -700 s- assuming modification depths as measured by UVSE. Table II.

Table II. Summary of as-deposited and 700 s He:H2 plasma treated film properties. The porosity change was calculated using LL equation, and mean pore size was measured by EP.

<table>
<thead>
<tr>
<th>Film</th>
<th>MD -UVSE -nm</th>
<th>DPR -mg/mm</th>
<th>EM -GPa -mean value</th>
<th>%RR %RI -top layer</th>
<th>LL porosity -top layer</th>
<th>Mean pore radii -top layer -nm</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Before</td>
<td>After</td>
<td>Before</td>
<td>After</td>
<td>Before</td>
<td>After</td>
</tr>
<tr>
<td>B2</td>
<td>69</td>
<td>0.0037</td>
<td>7.43</td>
<td>7.74</td>
<td>1.343</td>
<td>1.320</td>
</tr>
<tr>
<td>B3</td>
<td>150</td>
<td>0.0084</td>
<td>5.54</td>
<td>4.97</td>
<td>1.341</td>
<td>1.279</td>
</tr>
<tr>
<td>Ea</td>
<td>117</td>
<td>0.0137</td>
<td>4.48</td>
<td>2.84</td>
<td>1.378</td>
<td>1.226</td>
</tr>
<tr>
<td>Eb</td>
<td>154</td>
<td>0.0120</td>
<td>3.8</td>
<td>2.54</td>
<td>1.339</td>
<td>1.230</td>
</tr>
</tbody>
</table>

s He:H2-plasma-modified ~dashed lines~ films are shown in Fig. 5. The refractive indexes and extinction coefficients are different from film to film. According to recent results reported by Marsik et al.,15,16 absorption bands located between 200 and 300 nm are related to the presence of amorphous carbonlike porogen residues. Therefore, the difference in the absorption spectra of these films is mainly related to the different amounts of porogen residues.

The films Ea and Eb were deposited in exactly the same conditions, but they were cured by light with different wavelengths. It is clear from Fig. 5 that the curing by light with ~200 nm ~Ea~ leaves less porogen residues. Plasma exposure completely removed the porogen residue from both Ea and Eb films, and the final absorption spectra became similar to the UV spectra of the low-k matrix material. The refractive indexes of these two films after the porogen residue removal are the same. This is additional proof that all porogen residues were removed independently on the wavelength of UV light used for curing.

The low-k films B2 and B3 were deposited in the same PECVD chamber and cured by the same broad-band lamp with ~200 nm ~Table I~. However, they have different porosities that were provided by different ratios of the matrix and porogen precursors. Both these films contain less porogen residues in comparison with the films Ea and Eb. The film B3 has a higher porosity ~Table I~ and contains more porogen residues in comparison with B2. The disappearance of absorption bands between 200 and 300 nm for He:H2-treated films B2 and B3 indicates a complete removal of the porogen residues. However, the complete porogen residue removal for B2 and B3 films results in smaller changes in refractive indexes than for Ea and Eb films. This fact suggests that the relatively low porosity and pore size of the films Ea and Eb ~see Table II~ were defined by a large amount of porogen residue deposited on the pore wall.

The reduction of the refractive index ~RI~ suggests an increase in porosity. Therefore, the damage-free strip based on the He:H2 plasma could significantly change the films’ properties if the deposition and curing conditions were not sufficiently optimized ~i.e., leaves too much porogen residue~. One of the most expected problems related to porogen residue removal can be a change in the mechanical properties that directly depend on porosity.

Mechanical properties.— The amount of the removed porogen residue and the corresponding change in the films’ properties after 700 s of He:H2 DSP plasma exposure are summarized in Table II. The change in mass related to porogen residue removal ~Fig. 4~ was normalized to the thickness of the top modified layer ~MD in Table II~. The degree of porogen removal ~DPR~ was the highest for the Ea film ~0.0 137 mg/nm~ and approximately 3.7 times lower for the B2 film with the lowest porogen content ~0.0037 mg/nm~. The porosity was calculated using the Lorentz–Lorenz ~LL~ equation, assuming that the removed porogen has an RI value close to the film skeleton ~the first approximation~. The porosity is increased in all cases ~for all films~.

The mechanical properties of low-k films were evaluated using NI. Because the film thicknesses were relatively small ~Table I~, only a relative study was possible due to the Si substrate effect.~ NI showed a reduction in the EM for all films except B2 ~Fig. 6~. Film B2 has the lowest porogen residue content, as indicated by both UVSE and mass balance measurements ~Fig. 5 and 4~. The cause of the lower level of porogen residue is the lower porosity ~less porogen was used during deposition~ and optimized deposition and curing conditions in comparison with the films Ea and Eb. The film Ea with the highest porogen residue content shows the highest relative reduction in EM. The reduction in mechanical properties during the exposure to the He:H2 DSP plasma is proportional to the initial porogen content in the low-k material. Furthermore, the initial mechanical properties of films Ea and Eb are very much determined by...
porogen residues. Porogen residues provide relatively high EM, although the skeleton of these films is much softer than that of films B2 and B3.

The mechanical strengthening of silica-based porous materials by C-based polymer additions was already discussed by Zhang et al.59 Furthermore, Maidenberg et al.60 found that controlled porogen decomposition during the UV-curing process improves the fracture energy of methylsilsesquioxane low-\(k\) materials. However, this article reports on the modification of the CVD low-\(k\) mechanical properties due to the removal of porogen residue during the damage-free plasma processing.

Conclusions

The time effect of the He/H2 downstream ash plasma at 280°C on CVD low-\(k\) dielectric films with different porosities is evaluated. All films contain different amounts of porogen residue. The porogen residue is a nonvolatile product of UV photochemical dissociation of porogen with a chemical composition close to amorphous carbon and carbon-rich hydrocarbons. The amount of porogen residue depends on \(\sim v\) the deposition conditions and porosity. If more porogen is used during the deposition to get more porous films, more porogen residue remains after the curing. It also depends on \(\sim v\) the UV-curing conditions. The curing process with a wavelength of 172 nm generates more residues than the curing process with a wave-length longer than 200 nm.

The porogen residue can be removed by He/H2 plasma. The depth of removal is determined by the penetration depth of the H radicals into low-\(k\) materials. The porogen depleted layer becomes more porous, which is reflected in the mass loss, and the optical properties change after the plasma treatment. The good mechanical properties of the blanket films can be provided by the presence of dense porogen residues. The removal of this residue by He/H2 plasma significantly reduces Young’s modulus, suggesting that the film matrix would not remain sufficiently stiff after a regular UV curing. The controlled degradation of the mechanical properties and change in pore size after He/H2 plasma presents additional challenges during the integration. Therefore, the problem of a damage-free strip must be solved in combination with the improvement of deposition precursors, conditions, and curing of low-\(k\) films.

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