Effects of cesium ion-implantation on mechanical and electrical properties of organosilicate low-k films

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ABSTRACT

The effects of cesium (Cs) ion-implantation on uncured and ultraviolet (UV)-cured plasma-enhanced chemical-vapor-deposited (PECVD) organosilicate low dielectric constant (low-k) (SiCOH) films have been investigated. The mechanical properties, including the elastic modulus and hardness, of the SiCOH low-k films are improved by up to 29.9% with Cs implantation, and further up to 51.8% after annealing at 400 °C in a N₂ ambient. These improvements in mechanical properties are attributed to an enhancement of the Si-O-Si network structure. The k-value of the SiCOH films increased slightly after Cs implantation, and increased further after annealing. These increases are attributed to two carbon-loss mechanisms, i.e. the carbon loss due to Si-CH₃ bond breakage from implanted Cs ions, and the carbon loss due to oxidation during the annealing. These results indicate that Cs ion implantation could be a supplement to or a substitution for the incumbent UV curing method for processing SiCOH low-k films.
Low dielectric constant (low-\(k\)) dielectrics are needed to meet the performance and power consumption requirements of modern integrated circuits. Typically, these low-\(k\) dielectrics are organosilicate glasses. They are generally made of silicon (Si), carbon (C), oxygen (O) and hydrogen (H), which are called SiCOH, SiOCH, or SiOC:H.\(^1\) To lower the value of \(k\) even more, sacrificial components, called porogens, are introduced and subsequently removed to form porous ultra-low-\(k\) dielectrics.\(^2,3\) Unfortunately, the introduction of pores significantly weakens the mechanical properties of the resultant porous dielectric and renders it susceptible to process-induced damage.\(^2,4\) As a result, such porous low-\(k\) dielectrics are extremely difficult to work with and pose significant challenges to continued scaling of integrated circuits.\(^5\)

Recent work in Japan\(^6\) demonstrated surprising improvements of the electrical properties, mechanical properties, and reliability of porous silica films with the addition of a cesium (Cs) salt during the synthesis of porous low-\(k\) films using a wet method. That is, adding Cs, although it appears to be counter-intuitive, makes the dielectric better!

In contrast to the aforementioned porous-silica film being formed with wet chemistry, SiCOH as a mainstream interlayer dielectric (ILD) can only be prepared with plasma-enhanced chemical-vapor deposition (PECVD) in order to be integrated with other processes.\(^2\) At the present time, curing SiCOH using ultraviolet (UV) radiation offers some improvement in mechanical properties.\(^7,8\) However, there are tradeoffs. For example after UV exposure beyond what is needed to remove the porogens, the \(k\)-value begins to increase. In addition, carbon loss, which results in an increase in defect concentration, also occurs simultaneously.\(^9-11\)
In this work, the effects of a “dry” Cs ion-implantation in SiCOH are investigated. The goal is to determine whether the advantages previously obtained using wet chemistry could be obtained using Cs ion-implantation, thus being a potential supplement to or even a substitution for the incumbent UV curing method.

Two types of nonporous SiCOH low-k films deposited on (100) Si substrates with PECVD were used in this work; One set of films was uncured and the other was UV cured\textsuperscript{12}. Neither of these two films had porogens involved in their forming process. Three uncured film samples were implanted with Cs ions under three different conditions. The cured film was not implanted, but used as a comparison. The film properties and implantation conditions are summarized in Table I. Note that the unimplanted samples are labeled with letters A and B, while the implanted samples are labeled with numbers 1 to 3. The Cs doses were chosen such that the relative atomic concentrations in the low-k film varied from 20 to 200 ppm, assuming a uniform Cs distribution within the film. The ion-implantation energy was chosen to be 100 keV, based on a TRIM-code simulation\textsuperscript{13}. The simulation predicted that 100-keV Cs ions have a projected range between 100 and 110 nm. This range is approximately in the center of the film. All the implanted samples were subsequently annealed in an atmospheric-pressure nitrogen ambient for one hour at 400°C, in order to redistribute the Cs atoms more uniformly within the film.

Ellipsometry was used to measure the film thickness after each step of the procedure. Figure 1 shows the results. It can be seen that all the implanted films shrank slightly after implantation, and shrank even more after annealing. This matches the observations in previous work using the wet chemistry.\textsuperscript{6}
Nanoindentation was used to measure the elastic modulus and hardness of the films. Details of this technique can be found in a previous publication.\textsuperscript{14} Figure 2 shows the results. The horizontal axis, $h$, is defined as

$$h = \frac{\sqrt{\text{contact area}}}{\text{film thickness}},$$

where the contact area is the area of the indenter tip actually in contact with the film. Note $h$ is dimensionless. This provides a way to compare samples of different thicknesses. The vertical axis is either the effective modulus or the hardness of the samples. By effective modulus, we mean, that the measured modulus has contributions from the combination of the film and the substrate. These quantities are both functions of the load force. Note that at high loads (right half of the curves), all the measured curves (solid lines) tend to meet each other. This occurs because if the indent is deeper, the silicon substrate contributes dominantly to the measured values. Thus, the data points in the low-load region (left half of curves) can better measure the film properties, since under these loads, the effect of the substrate is minimal.\textsuperscript{14}

The hardness and modulus data for each sample were averaged over the range of $h$ between 1.2 and 2.0. The results are shown in Table II. It can be seen that all the Cs-implanted samples (Samples 1, 2 and 3) show improved elastic modulus and hardness compared with Sample A (uncured unimplanted). The more heavily doped samples show greater improvement, up to 56 percent, in both mechanical properties, especially after annealing. Furthermore, after annealing, Samples 2 and 3 exhibit a comparable elastic modulus and hardness compared with Sample B (UV cured unimplanted).

Note that the above method reveals only the \textit{relative} improvements of the mechanical properties from Cs-implantation and annealing. The true elastic modulus, which is an intrinsic
property of the film itself, cannot be determined using this method.\textsuperscript{14-16} A possible technique to determine the absolute value of the elastic modulus is proposed here by utilizing a model developed by Stone.\textsuperscript{15} The model uses the substrate properties along with a range of possible absolute elastic moduli of the film to obtain a set of parametric curves. In Figure 2(a), the curves based on Stone’s model (hollow symbols) are plotted. In principle, by comparing the experimental curves in the low-load region to the parametric curves, one may determine the true elastic moduli of the film.\textsuperscript{14} However, because of the small thicknesses of the films, it was not possible to obtain sufficient data in the low-load region to determine the modulus directly. Thus, the averaging method described above was used to demonstrate the improvement of the film mechanical properties.

To understand the basis for these improvements, Fourier-Transform Infra-Red spectroscopy (FTIR) measurements were used to analyze the Si-O bond configuration in the film. The results are shown in Figure 3. The peak around 1140 cm\textsuperscript{-1} represents the Si-O-Si cage structure and the peak near 1065 cm\textsuperscript{-1} represents the Si-O-Si network structure.\textsuperscript{17} It can be seen that compared with Sample A (uncured unimplanted film), the Cs-implantation changes the majority of the Si-O-Si bonds from being a cage structure to a network structure. Higher Cs doses lead to a higher network-structure peak. This change contributes to the improvement of the mechanical properties.\textsuperscript{3,5}

To examine the electrical properties of these films, Capacitance-Voltage (C-V) measurements, utilizing a metal dot/dielectric/silicon structure and a pin-probe station, were performed to find the $k$-value of the samples. The setup details can be found in a previous publication.\textsuperscript{18} The measurement was done in ambient air and humidity. The results are also
shown in Table II. It can be seen that all the implanted samples experienced a small increase in $k$-values after implantation, and developed an even higher value after annealing.

According to reported results\textsuperscript{3,5} for SiCOH dielectrics, carbon loss, especially Si-CH$_3$ bond loss, can lead to $k$-value increases. This loss of Si-CH$_3$ bond is confirmed in this work with FTIR and X-ray Photoelectron Spectroscopy (XPS) depth profiles. The FTIR results are shown in Figure 4. The peak around 1274 cm$^{-1}$ represents Si-CH$_3$ bonds\textsuperscript{17}. It can be seen that more Cs doping leads to slightly lower levels of Si-CH$_3$ bonds. This is likely to be due to the fact that implanted Cs ions can break Si-CH$_3$ bonds during deceleration and thus cause carbon loss, since the Si-CH$_3$ bonds are much weaker than the Si-O bonds (4.7 eV vs 8.3 eV)\textsuperscript{5}.

The XPS depth profile results, \textit{e.g.} comparisons between Samples A, 3, and B are shown in Figure 5. It can be seen that the unimplanted Samples A and B have constant atomic compositions through the entire depth of the film. Sample B shows a uniform carbon loss compared with Sample A because it has been UV-cured. In contrast, the as-implanted but not annealed Sample 3 shows a carbon loss within the top half of the film. This can be attributed to the implanted Cs ions as described above. The implanted and annealed Sample 3 shows additional carbon loss through the entire thickness of the film. This can be attributed to oxidation after the samples were removed from the annealing furnace. The inverse relationship between the oxygen and carbon XPS depth profiles indicates that oxygen atoms take the place of carbon atoms. Note that the extra oxygen can also explain the overall increase of the two Si-O-Si peaks shown in Figure 3. In Figure 5, by comparing as-implanted but not annealed Sample 3 with Sample B, it can be seen that Cs implantation and UV curing produce similar levels of overall carbon loss. Given the reasons for the two mechanisms of carbon loss in Sample 3, it is reasonable to believe that reducing the implantation energy for thinner films than those used here
while optimizing the annealing conditions, may also help to suppress both the carbon loss and the concomitant increase of the $k$-value.

Finally, time-zero dielectric breakdown (TZDB) characteristics were measured with the same system used for C-V measurements, except that the LCR meter was replaced with a picoammeter. Each sample was tested 20 times at 20 separate metal dots that were deposited on the sample. The box-plot\textsuperscript{19} statistics of the TZDB characteristics are shown in Fig. 6. It can be seen that for as-implanted samples, implanted Cs atoms did not cause significant degradation to the TZDB voltage. In fact, this may improve the TZDB voltage. Except for Sample 3, it appears that the as implanted but unannealed samples have a higher TZDB voltage than the corresponding annealed samples and pristine Samples A and B. Conversely, the implanted and annealed Sample 3 shows a TZDB voltage higher than the as-implanted unannealed Sample 3, as well as pristine Samples A and B.

In summary, the effects of dry Cs-ion implantation on the mechanical and electrical properties of uncured nonporous low-k SiCOH films have been investigated, and compared with UV-cured nonporous SiCOH film. The elastic modulus and hardness of the SiCOH films were found to improve with increasing Cs dose. This improvement is more significant for annealed samples. Two higher-dose samples show comparable elastic moduli and hardness to the UV-cured film. The improvement of the mechanical properties is attributed to an enhanced network structure of the Si-O-Si bonds. The $k$-values of the low-$k$ films were found to increase lightly after Cs implantation, and to increase further after annealing. This increase is attributed to carbon loss in the film. Two mechanisms of carbon loss require optimization of implantation and annealing conditions. For low and medium Cs doses, the TZDB voltages of as-implanted but
unannealed samples are actually higher compared with pristine samples. However, for high Cs doses, an implanted and annealed sample shows a higher TZDB voltage than that for the pristine samples. Based on the above, the medium or high Cs dose implantation has the potential to be a supplement to or substitution for the incumbent UV curing method in terms of improving the quality of the nonporous SiCOH film.

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REFERENCES


TABLES

TABLE I. Properties of pristine films and Cs ion-implantation conditions.

<table>
<thead>
<tr>
<th>Film type</th>
<th>Thickness (nm)</th>
<th>Nominal k-value</th>
<th>Sample label</th>
<th>Cs ion dose (ions/cm²)</th>
<th>Cs ion energy (keV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Uncured</td>
<td>233.1</td>
<td>3.2</td>
<td>Sample A</td>
<td>N.A.</td>
<td>N.A.</td>
</tr>
<tr>
<td>Uncured</td>
<td>234.0</td>
<td>3.2</td>
<td>Sample 1</td>
<td>$1 \times 10^{13}$</td>
<td>100</td>
</tr>
<tr>
<td>Uncured</td>
<td>231.9</td>
<td>3.2</td>
<td>Sample 2</td>
<td>$5 \times 10^{13}$</td>
<td>100</td>
</tr>
<tr>
<td>Uncured</td>
<td>233.4</td>
<td>3.2</td>
<td>Sample 3</td>
<td>$1 \times 10^{14}$</td>
<td>100</td>
</tr>
<tr>
<td>UV-cured</td>
<td>211.4</td>
<td>3.2</td>
<td>Sample B</td>
<td>N.A.</td>
<td>N.A.</td>
</tr>
</tbody>
</table>
### TABLE II. Averaged mechanical properties (data points that have $1.2 < h < 2.0$), and $k$-values.

<table>
<thead>
<tr>
<th>Sample label</th>
<th>Averaged effective modulus (GPa)</th>
<th>Relative change (%)</th>
<th>Averaged hardness (GPa)</th>
<th>Relative change (%)</th>
<th>Normalized $k$-values</th>
<th>Relative change (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>P-A</td>
<td>33.6</td>
<td>N.A.</td>
<td>2.13</td>
<td>N.A.</td>
<td>3.2</td>
<td>N.A.</td>
</tr>
<tr>
<td>I-1</td>
<td>34.7</td>
<td>+3.04</td>
<td>2.22</td>
<td>+3.88</td>
<td>3.22</td>
<td>+0.47</td>
</tr>
<tr>
<td>I-2</td>
<td>41.1</td>
<td>+22.1</td>
<td>2.37</td>
<td>+11.0</td>
<td>3.75</td>
<td>+17.1</td>
</tr>
<tr>
<td>I-3</td>
<td>43.7</td>
<td>+29.9</td>
<td>2.46</td>
<td>+15.5</td>
<td>3.75</td>
<td>+17.1</td>
</tr>
<tr>
<td>A-1</td>
<td>40.5</td>
<td>+20.3</td>
<td>2.64</td>
<td>+23.9</td>
<td>3.32</td>
<td>+3.76</td>
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<tr>
<td>A-2</td>
<td>50.2</td>
<td>+49.1</td>
<td>2.95</td>
<td>+38.4</td>
<td>3.77</td>
<td>+17.8</td>
</tr>
<tr>
<td>A-3</td>
<td>52.6</td>
<td>+56.5</td>
<td>3.02</td>
<td>+41.5</td>
<td>3.90</td>
<td>+22.0</td>
</tr>
<tr>
<td>P-B</td>
<td>46.3</td>
<td>N.A.</td>
<td>2.95</td>
<td>N.A.</td>
<td>3.2</td>
<td>N.A.</td>
</tr>
</tbody>
</table>

Sample labels: P- pristine, I- as implanted but not annealed, A- implanted and annealed.

Samples A, 1, 2, and 3 are uncured SiCOH films. Sample B is UV-cured SiCOH film.
FIGURE CATIONS

Fig. 1 Ellipsometry measured film thicknesses

Fig. 2 Nano-indentation measured (a) effective modulus and (b) hardness. Simulation curves are also shown in (a) as hollow symbols.

Fig. 3 FTIR measured Si-O bonds for Type A series.

Fig. 4 FTIR measured Si-CH3 bond for Type A series.

Fig. 5 XPS depth profiles for Type A series and pristine Type B film.

Fig. 6 TZDB box-plot statistics for Type A series and pristine Type B film