Restoration and pore sealing of plasma damaged porous organosilicate low $k$ dielectrics with phenyl containing agents

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Silylation-based techniques are being actively investigated for dielectric recovery after plasma processing of porous ultralow dielectric constant (low $k$) dielectrics. A two-step pore sealing and dielectric recovery process was attempted on plasma damaged porous organosilicates (OSG). In the sealing step, an OSG low $k$ monomer, phenyltrimethoxysilane, was used to form a thin low $k$ sealant layer. Scanning transmission electron microscopy and transmission electron microscopy images indicated a much improved low $k$/barrier interface as a result of pore sealing. In the surface silylation step, two phenyl-containing agents, diphenyltetramethyldisilasane and phenyltrimethoxysilane, were employed to restore surface hydrophobicity. The process was found to be capable of restoring surface hydrophobicity and partially blocking the pathway for moisture adsorption without much adverse effect on the subsequent atomic layer deposition of Cu barrier. © 2007 American Vacuum Society. [DOI: 10.1116/1.2738489]

I. INTRODUCTION

The further delay in the introduction of porous ultralow $k$ (ULK) dielectrics according to various revisions of the roadmap1 is simply an acknowledgment of severe challenges facing ULK integration. Due to weak mechanical strength and poor resistance against chemical and plasma damage, porous organosilicate low $k$ dielectrics are susceptible to damage induced during etch/ashing/clean processes, resulting in degraded dielectric and electrical properties and aggravated surface roughness.2–4 As plasmas break the weakly bonded organic terminal groups from the silica backbone and densify the porous medium with further cross linking, a silicaceous damaged “skin” layer is formed.5,6 If there are no quick breakthroughs in either patterning processes or ULK property enhancement, the dielectric degradation may limit further scaling of the low $k$ dielectrics. There are severe yield and reliability concerns also. Embedded charged ions and dangling bonds induced in the plasma processes create defective and electrically active sites that can provide additional conduction mechanisms in the presence of electric fields. An aggravated surface roughness of patterned low $k$ or ULK makes it difficult to achieve continuous barrier coverage at acceptable thickness.

Much effort is being dedicated to minimizing such damage in the first place.7,8 As a second choice, postpatterning remedies have also been explored. Surface silylation of damaged ULK dielectrics is one of such remedies intended for dielectric recovery and surface planarization or pore sealing which may become essential for the successful implementation of porous ULK dielectrics.

One approach of surface silylation for dielectric recovery is to use trialkyl-substituted disilazanes or chlorosilanes, such as hexamethyldisilazane (HMDS) and trimethylchlorosilane (TMCS), and so on.9–11 While these silylation agents have been confirmed to partially recover the dielectric damage, they are inadequate for surface planarization/pore sealing due to only monolayer coverage. And there are also concerns of detrimental effects on the subsequent barrier processes with atomic layer deposition (ALD), because the final surface after silylation is terminated with methyl bonds which are inactive in ALD nucleation process.12,13

In this work, a novel silylation process has been attempted to tackle these Cu/low $k$ interface engineering issues from an integration point of view. The surface silylation is designed to selectively attack the silanol bonds induced in plasma processes, while at the same time introducing cross-linking bonds for pore sealing and surface planarization and also attempting to provide surface nucleation sites for ALD barrier processing. For this purpose, a two-step silylation process is proposed: first the deposition of cross-linked organosilicate sealant layer with phenyltrimethoxysilane (PTMOS) for pore sealing and surface planarization, followed by a surface finish with phenyl containing trisubstituted silylation agents, such as phenyltrimethoxysilane (PDMCS) and diphenyltetramethyldisilazane (DPTMDS), for dielectric recovery and to introduce benzene groups at the surface as the ALD nucleation sites13 and to passivate the surface silanol groups against moisture uptake.

II. EXPERIMENT

The generic reaction mechanisms for silylation are given as follows:

(a) \[ \text{Si} - \text{OH} + R_2\text{SiR'} - \text{NH} - R' \text{SiR}_2 \rightarrow \text{Si} - \text{O} - R_2\text{SiR'} + \text{NH}_2 - R' \text{SiR}_2, \]

(1)

(b) \[ \text{Si} - \text{OH} + R_2\text{SiR'} - \text{Cl} \rightarrow \text{Si} - \text{O} - R_2\text{SiR'} + \text{HCl}. \]

(2)
As a preliminary study, all the surface silylation experiments were carried out with wet chemistry in a ventilated hood. Novel dielectric recovery agents, such as PDMCS and DPTMDS, were obtained from Gelest. Other silylation agents more commonly used, such as TMCS and HMDS, were obtained from Sigma-Aldrich.

The dielectric recovery and pore sealing process was demonstrated on a mesoporous organosilicate low k film with a mean pore size of 2.4 nm, a thickness of 3000 Å, and a dielectric constant of 2.2. This low k film was first damaged with a low power (100 W) Ar balanced O2 plasma process to simulate the plasma damage that may occur during etch/ashing/clean processes.

To control the moisture in all the experiments, damaged low k samples were baked at 120 °C for more than 2 h before silylation. The samples were then put in a stirred solution of silylation agents maintained at 80 °C for various time periods. They were removed from the solution and rinsed with corresponding solvents to remove residues of the silylation agents. Some of the samples were postbaked at 200 °C to achieve better dielectric recovery.

Chemical modifications induced by plasma processing and the subsequent silylation were monitored with Fourier transform infrared spectroscopy (FTIR) using a Thermo Nicolet Magna-IR 560 spectrometer, and with x-ray photoelectron spectroscopy (XPS) using a Leybold-Heraeus system. Details of the XPS system can be found elsewhere. Since FTIR is not a surface sensitive technique, the Ar/O2 plasma damaging process was intentionally overdone up to 10 min to illustrate the changes in the IR absorbance characteristics.

Surface hydrophobicity was studied with contact angle measurements using a Ramé-Hart CA100 goniometer. Contact angle measurements were done with three liquids: water, glycerol, and diiodomethane in order to separate the polar and nonpolar surface energies.

The change in the dielectric and electrical properties was studied with metal-insulator-semiconductor (MIS) capacitors formed by shadow masked Al/Cu sputtering. Capacitance-voltage and leakage-voltage data were collected on these MIS capacitors.

The interaction between the silylation process and ALD Ta3N5 barrier process was studied in an integrated ultrahigh vacuum (UHV) system which enables in situ surface chemical investigation of the ALD barrier process. 150 identical ALD Ta3N5 cycles with a nominal thickness of 4 nm were deposited on three repaired plasma damaged porous organosilicate (OSG) samples: one with only sealant deposition, one with sealant and TMCS finish, and one with sealant and PDMCS finish.

III. RESULTS AND DISCUSSIONS

The effect of chemical modifications due to the plasma process on the FTIR spectra is presented in Figs. 1–3. After the extremely damaging process, Si–CH3 deformation at 1276 cm−1 and aliphatic C–H stretches at 2800–3000 cm−1 almost disappeared, and silanol groups (960 cm−1), surface hydroxyl (3750 cm−1), and associated broad hydroxyl band around 3600 cm−1 due to moisture absorption on the silanol sites increased. This is expected as plasma damage in low k films usually results from depleting methyl groups bonded with silicon and creating more dangling Si bonds. In the presence of moisture, these dangling bonds form silanol groups, and moisture can be further physisorbed on the polar silanol groups. The adsorbed moisture and the increased silanol termination both contribute significantly to the dielectric
loss, i.e., the increase of the dielectric constant.\textsuperscript{20-22} The shift in Si–O–Si asymmetric stretches at 980–1260 cm\(^{-1}\) is usually interpreted as a plasma densification effect: the transformation of low bond angle suboxide around 1035 cm\(^{-1}\) to higher bond angle Si–O–Si network at 1070 cm\(^{-1}\).\textsuperscript{23} As a result of silylation of the damaged ULK film with DPTMDS catalyzed with PDMS, aliphatic C–H stretches at 2800–3000 cm\(^{-1}\) and Si–CH\(_3\) deformation at 1276 cm\(^{-1}\) increased slightly, indicating incorporation of more organic groups bonded with silicon. The increased Si–O–Si absorbance peaks after silylation can be attributed to the condensation of silanol groups during the dehydration bake.

The evidence for incorporation of benzene structures on the surface was not very obvious due to low concentration and overlapping with other absorption bands. Nevertheless, the observed additional IR absorption bands at 3020–3080 cm\(^{-1}\) may be interpreted as \(\mathrm{C–H}\) stretches in the phenyl (Ph) group bonded with silicon and the two little kinks at 1255 and 1120 cm\(^{-1}\) can be interpreted as Si–CH\(_3\) deformation in PhSi(CH\(_3\))\(_2\) and Si–Ph stretch, respectively.\textsuperscript{24} The slight increase in absorption at 730 cm\(^{-1}\) might also be interpreted as out-of-plane ring vibration in Si–Ph bonds.\textsuperscript{24} This is accompanied by an increase of Si–C stretch in Si(CH\(_3\))\(_2\) bonds at 800 cm\(^{-1}\).\textsuperscript{24} In the corresponding XPS C 1s evolution presented in Fig. 3, small peaks which can be interpreted as \(\pi-\pi^*\) shake-ups started to appear at \(-290\) to \(-292\) eV after silylation.

Surface silylation was more conclusively shown with the surface energy results derived from the contact angle measurements. Using three liquids, the contact angles were measured on the untreated film, film after the plasma process, and film after the subsequent silylation process. Applying the Young-Dupré equation, the polar and dispersive surface energy terms were extracted. The results are tabulated in Table I.

The recovery of surface hydrophobicity is very clear with the changes of the contact angle of water on the pristine surface, the plasma damaged surface, and the silylated surface. The contact angle was more than 80° on the original film as it was very hydrophobic. After the plasma process, more polar silanol groups and dangling bonds were generated on the surface, so the contact angle decreased dramatically to a value beyond the detection limit. After the silylation process, the contact angle was almost completely recovered. Correspondingly, the polar surface energy increased considerably from 4.7 erg/cm\(^2\) of the untreated film to 23.2 erg/cm\(^2\) due to the plasma damage and was reduced significantly back to 8.3 erg/cm\(^2\) resulting from the surface silylation. Consequently, surface hydrophobicity is expected from the silylated film.

Silylation attempts to address specifically the root cause of dielectric degradation: methyl depletion and induced hydrophilicity. With the addition of hydrophobic methyl termination, surface hydrophobicity can be recovered. However, only a slight decrease of free hydroxyl groups was observed. This can be attributed to water absorption before or after silylation. Similar observations were reported by other researchers.\textsuperscript{25} Surface hydrophobicity only prevents moisture adsorption on the surface but does not guarantee the elimination of pathways for moisture penetration.\textsuperscript{26,27} The loose molecular structure of porous low \(k\), in general, and the interconnected pore structure of this mesoporous material, in particular, have provided such pathways for moisture penetration. As long as there are polar sites present in the bulk of the damaged low \(k\) film, moisture can eventually penetrate through the hydrophobic surface region and get adsorbed despite surface hydrophobicity after silylation.

Although there have been attempts to repair plasma damage deep in the bulk of porous low \(k\)’s,\textsuperscript{9,10} it is not really practical to completely remove the deep bulk damage considering the long time required to drive out the adsorbed moisture. The bulk damage is usually first mitigated by optimizing plasma processes. In case of severely damaged porous low \(k\) films as in this study, a mere monolayer coating simply could not block the moisture pathways formed during the plasma processes. Moreover, these silylation agents themselves are very sensitive to moisture. Without a deep dehydration prebake to drive out water molecules adsorbed on silanol sites in the bulk, the silylation of bulk silanol sites might not have been as effective. A complete dielectric re-

![Fig. 3. Evolution of XPS C 1s spectra during silylation experiments.](image)

<table>
<thead>
<tr>
<th>Contact angle</th>
<th>H(_2)O</th>
<th>Glycerol</th>
<th>Diodomethane</th>
<th>(y^p) (erg/cm(^2))</th>
<th>(y^{\text{Dis}}) (erg/cm(^2))</th>
</tr>
</thead>
<tbody>
<tr>
<td>Untreated film</td>
<td>83.8</td>
<td>85.1</td>
<td>54.5</td>
<td>4.7</td>
<td>26.9</td>
</tr>
<tr>
<td>Damaged</td>
<td>5.7</td>
<td>13.7</td>
<td>23.9</td>
<td>23.2</td>
<td>35.6</td>
</tr>
<tr>
<td>Silylated film</td>
<td>79.3</td>
<td>80.6</td>
<td>33.5</td>
<td>8.3</td>
<td>36.8</td>
</tr>
</tbody>
</table>
covery process in real applications may involve a certain thickness of densified layer formed either by changes to the plasma processes or adding blocking sealant layer before a hydrophobic finish with surface silylation or vice versa. The following section demonstrates that surface silylation by itself has been found to improve significantly the dielectric and electrical properties of the damaged porous low k film.

A. Evaluation of dielectric recovery effects

The effects of silylation on the dielectric constant and the leakage current were evaluated using standard MIS capacitors. The dielectric constant was derived from the capacitance at the accumulation using a parallel-plate capacitor model. The dielectric constants obtained are presented in Fig. 4. Because the films are highly porous and the film thickness was only around 3000 Å, plasma damage induced leakage made these capacitors very leaky. Most of the CV measurements failed due to degraded dielectric breakdown before arriving at the flat band voltage which was normally as high as −15 V or 0.5 MV/cm in terms of the electrical field. Only a few capacitors survived. The error bars given in the chart are conservatively estimated to be 10% based on historical data.

As shown in the chart above, the dielectric constant increased from 2.2 to 3.9 after a plasma process with 85/15 Ar/O2 ratio for 10 min. With dehydration bake, the dielectric constant could drop to 3.5 on the damaged film, indicating that the dielectric degradation was partly caused by moisture adsorption. After silylation of the damaged film in DPTMDS solution catalyzed with small amount of PDMCS, the dielectric constant decreased to 3.2. After additional dehydration bake at 200 °C, further decrease in the dielectric constant was observed. The final k value was 2.7 on the repaired surface indicating some degree of dielectric recovery.

The repair of plasma induced damage was more remarkable in the leakage current measurements. On the plasma damaged film, all the MIS capacitors became very leaky. Measured at −1.0 V reverse bias or at an electrical field of 0.03 MV/cm, the leakage current jumped from 0.1 nA/cm² to μA/cm² in the worst case. At bias higher than −1.0 V, the leakage current on some samples showed dielectric breakdown. Due to the large experimental scatter, only I-V curves on good samples are presented in Fig. 5. The plasma condition was 85 SCCM (SCCM denotes cubic centimeter per minute at STP)/15 SCCM Ar/O2 ratio at 100 W for 5 min. After the plasma treatment the leakage current was 88 nA/cm² due to plasma damage. After silylation, the leakage current was reduced by orders of magnitude to 0.26 nA/cm². A dehydration bake alone reduced the leakage current on the damaged sample to 23 nA/cm². However, only with silylation was the leakage current reduced to a level similar to what was on the untreated film. An additional dehydration bake had no significant effect on the leakage current.

To further investigate the dependence of the leakage current on the plasma conditions, four different plasma processes were performed on the same porous OSG film, followed by an identical silylation process and dehydration bake. The leakage currents measured at −1.0 V reverse bias are presented in Fig. 6.
When using the leakage current as a measure of damage, the plasma induced damage increased with O₂ partial pressure, dc bias (related to dc plasma power output), and process time. This was expected because the chemical effect by oxygen radicals and the physical impacts by energetic ions, especially the argon ions, are regarded as the main factors causing the damage.

On all the samples damaged in different plasma conditions, silylation reduced the leakage current by orders of magnitude. The dehydration bake helped reduce the leakage in the damaged films but did not further reduce the leakage in the silylated films. This observation revealed another important role of silylation: the passivation of dangling bonds on the surface and in the bulk. This could be the reason that dehydration bake was very effective in the recovery of the dielectric constant but not so effective in reducing the leakage current for dielectrics with interconnected pores.

B. Silylation based CVD organosilicate pore sealant

It was clear from the CV measurements that a monolayer silylation was not able to block moisture penetration into the bulk of the damaged mesoporous dielectric. Additional sealant is then required for both hermetic sealing and surface planarization.

Pore sealing was attempted using certain alkylsilsesquioxanes, such as PTMOS, on the damaged OSG films. These molecules can react with the surface silanol bonds to form Si–O–Si bonding with volatile alcohol by-products. They can also cross link among themselves through formation of Si–O–Si bonding with volatile ether by-products. The alkyl side groups act as cross-linking terminators to prevent the formation of a complete silica network. Anchored on the plasma damage induced surface silanol groups, a thin low k coating can be deposited to gradually bridge the pore openings. As the coating thickness increases, the porous surface is planarized and eventually sealed against precursor and moisture penetration. The mechanism is illustrated in Fig. 8.
The effect of pore sealing was examined with cross-section electron microscopy. A sample of the porous organosilicate film after the plasma process and a sample after the organosilicate sealant deposition were capped with ALD of Ta$_3$N$_5$ barrier. Since our porous low $k$ film did not withstand the high intensity focused electron beam, electron energy loss spectroscopy was not successful on these transmission electron microscopy (TEM) specimens. Only cross-section TEM and scanning transmission electron microscopy (STEM) images are presented in Fig. 9.

Direct ALD Ta$_3$N$_5$ barrier deposition on the Ar/O$_2$ plasma damaged porous OSG sample had a diffuse interface, which could be attributed to precursor penetration and intermixing due to the surface roughness. From the TEM cross-section image in Fig. 9(b), the diffuse interface thickness is about 5 nm or only two pore sizes thick. This suggests that the plasma damaged surface was already partially sealed. The penetration of Ta$_3$N$_5$ barrier was not very severe. With the additional sealant layer, a much better defined interface was observed between the sealant layer and the ALD Ta$_3$N$_5$ barrier [comparing Figs. 9(a) and 9(c)]. The improved interface is an indication of much less intermixing or penetration.

By varying deposition time, sealant layers of various thicknesses can be deposited. Pore sealing has been achieved with a sealant of thickness less than 10 nm. The impact of the sealant layer on the dielectric property of the porous low $k$ was not evaluated. Since the sealant thickness is only a very small portion of the whole film thickness and the sealing agents themselves are monomers used in the OSG low $k$ synthesis, the change of the dielectric constant is difficult to detect.

A rough estimation can be made assuming a $k$ value of 2.2 for future porous ultralow $k$ and a serial parallel capacitor model for the contribution of the sealant layer, the maximum increase in the dielectric constant due to the additional 10 nm sealant layer on a 100 nm porous low $k$ can be estimated as

$$
\Delta k = \frac{d_{\text{seal}}/k_{\text{ULK}}}{d_{\text{ULK}}/k_{\text{ULK}} + d_{\text{sealant}}/k_{\text{sealant}}} - 1
$$

$$
= \frac{110/2.2}{100/2.2 + 10/2.8} - 1 \approx 2 \%	ag{3}
$$

It is clear from the reaction chemistry that the sealing agents cannot remove the plasma induced silanol groups, but the incorporation of additional methoxyl or ethoxyl groups and alkyl side groups may help passivate the damaged sites in the bulk. When moisture is driven out before the pore sealing process, the sealant layer can also serve as a blocking layer against moisture penetration. But the final surface contains plenty of siloxane groups which may turn into silanol groups through hydrolysis. Additional surface finish will be needed to achieve a hydrophobic surface.

C. Impact on ALD barrier process

As mentioned above, surface silylation and pore sealing processes can be complementary in achieving desired surface hydrophobicity and resistance against precursor and moisture penetration. A complete pore sealing and dielectric recovery process was thus proposed with silylation based chemical vapor deposition (CVD) of an organosilicate sealant layer followed by surface silylation with phenyl-containing agents to create a hydrophobic surface.

A study of this final surface for porous low $k$ patterning was focused upon its impact on the subsequent ALD barrier deposition. Two surface finish processes after a pore sealing process were compared, one with trimethylchlorosilane (TMCS) and the other with phenyldimethylchlorosilane (PDMCS). These chemicals are generally regarded as incompatible with Cu/OSG low $k$ processes due to corrosion and etching by HCl by-products. However, unlike the more process compatible HMDS and DPTMDS, TMCS and PDMCS have better reaction rates. The film surface silylated with TMCS has much more methyl termination than that silylated with PDMCS. The growth behaviors of ALD Ta$_3$N$_5$ on these two types of surface chemistry were examined to illustrate the impacts of surface silylation on ALD barrier process. The corresponding XPS Ta 4$p$ and N 1$s$ spectra are presented in Fig. 10.

As evidenced by the decrease of Ta 4$p$ and N 1$s$ peak heights, the ALD growth rate was almost halved after surface silylation with TMCS. In contrast, the deposition rate was almost the same after surface silylation with PDMCS. This difference can be attributed to the ability of the silylation agents to incorporate benzene rings for ALD nucleation sites. Since ALD barrier processes are sensitive to surface chemistry, improper silylation agents applied following the pore sealing step to recover the dielectric constant can adversely affect the subsequent ALD barrier process.
IV. SUMMARY

In summary, a novel surface treatment based upon surface silylation was investigated for pore sealing, dielectric recovery, and its impact on ALD Ta$_3$N$_5$ barrier process. This process involved the use of organosilsesquioxanes for pore sealing followed by surface finish with phenyl-containing silylation agents.

On porous organosilicate (OSG) surfaces damaged with various Ar/O$_2$ plasma processes, surface silylation was demonstrated with diphenyltetramethyldisilazane (DPTMDS) catalyzed with PDMCS. The silylation process was observed to significantly reduce the dielectric constant and considerably reduce the leakage current. Less than 10 nm thick organosilicate sealant layer had a clearly defined interface with ALD Ta$_3$N$_5$ barrier showing no intermixing in cross-section TEM images.

Effects of dehydration bake on the dielectric and electric properties of the plasma damaged porous OSG samples and silylated samples were also studied. Since the dehydration bake usually has a positive effect on the damaged samples while not very effective on the silylated samples, the role of silylation is most likely to passivate the damage-induced polar sites and broken bonds on the surface and in the bulk and recover surface hydrophobicity. Even though it cannot remove the damage-induced polar silanol groups, the passivation of these moisture adsorptive sites is one of the best remedies available. Because monolayer coverage cannot serve as a hermetic sealant when the mean pore size is large, a near hermetic surface can be achieved through a silylation-based CVD sealant followed by hydrophobic surface treatment.

However, a hydrophobic surface is often not conducive to ALD barrier processes. A high degree of methyl termination as in the case of HMDS silylation process is detrimental to ALD barrier nucleation. To overcome this difficulty, surface treatment with phenyl containing silylation agents has been used. It was demonstrated that a hydrophobic surface, passivated interface dangling bonds, and retention of the surface activity for ALD nucleation can be achieved.

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