As microelectronic circuits become smaller, the connections between the transistors have a greater influence on the circuit performance than the devices themselves. Interconnect performance is determined by the product of R, the resistance of the metal lines, and C, the capacitance of the intermetal dielectric. Due to its low resistivity, copper has replaced aluminum to reduce the R. Similarly, C can be reduced by replacing SiO₂ insulator (k = 4.2) with a low-k material. In addition, a-SiO₂:H film as a diffusion barrier having lower k value has been proposed to lower the capacitance. Carbon-containing low-k films, however, present the problem of a hydrophobic surface, which is difficult to rinse and dry without creating watermarks or leaving undesirable surfactant residue.

A common method for low-k film deposition is chemical vapor deposition (CVD). As one of the CVD-based candidates, a-SiO₂:H films have aroused interest due to their compatibility with very large scale integration (VLSI) and their low dielectric constant. By co-depositing a porogen molecule with a dielectric precursor, one can generate micro-pores in a film upon post deposition annealing; accordingly, the removal of thermally unstable methyl (CH₃) fractions during the annealing is one of the essential steps toward lowering the dielectric constant of low-k films. It is why various porosity-increasing methods have been proposed such as a conventional furnace annealing, a hydrogen plasma treatment, a diluted HF solution dipping, and a UV cure annealing. However, there has been limited study on various annealing ambient effects on low-k films. In conjunction with the hydrophobicity/hydrophilicity changes on the film surface, it is important to thoroughly understand gas ambient annealing effects on the electrical and structural behaviors of low-k films. It is also helpful to understand fundamental properties of low-k films. In this paper, we focused on the changes in the properties of the film and the dielectric constant. We also proposed the optimized annealing condition to solve the problem of hydrophobic surface inherently caused by carbon in the film.

Low-k a-SiO₂:H films were deposited by an inductively coupled plasma-type plasma-enhanced chemical vapor deposition (PECVD) method using bis-trimethylsilylmethane (BTMMS, H₃C₂-Si-CH₃) precursor. The precursor was vaporized and carried with an inert Ar gas at a flow rate of 2 sccm from a thermalista baffler, maintained at 35°C, to the reaction chamber. Argon and O₂ were used as dilute and oxidant gases, respectively, and the flow rates of those gases were both 30 sccm. Meanwhile, the processing pressure was 0.2 Torr and plasma power was 80 W. The deposition temperature was fixed at 25°C.

To investigate different gas ambient annealing effects, annealing was conducted under four different conditions: N₂ (hereafter sample N), a forming gas 1 (5% H₂ + 95% N₂, sample F₁), a forming gas 2 (10% H₂ + 90% N₂, sample F₂), and O₂ (sample O) ambients. It was performed at 450°C for 30 min in a conventional furnace. We used a hydrogen-nitrogen mixture gas instead of pure hydrogen which cannot be used due to its highly explosive nature. For C-V measurements, we modified the annealing sequences so that we can obtain more prominent annealing ambient effect in C-V curves; all as-deposited samples were annealed at 450°C in an N₂ ambient, and Al (or Pt for the sample O), a top electrode, was E-beam evaporated, followed by the final four different annealing processes at 400°C.

The out-gassing analysis of the as-deposited and the sample N was carried out using the thermal desorption spectroscopy (TDS). The samples were heated from room temperature to 900°C with a heating rate of 5°C/min. The structure of the films was analyzed with X-ray photoelectron spectroscopy (Axis, Kratos) and the take-off-angle of 90° was used for all analyses. The adventitious hydrocarbon part (C-C/H) of the carbon line was set at 284.9 eV when performing a binding energy calibration. Fourier transform infrared spectroscopy (FTIR) measurements were performed on a Jasco FT/IR-660 plus spectrometer in absorption mode at 4 cm⁻¹ resolution. Water contact angle measurement was performed on a SEO Phoenix-300. It is a powerful tool with which one can easily check the surface hydrophobicity/hydrophilicity.

Figure 1a presents the FTIR spectra of the as-deposited sample and the samples N, F₁, F₂, and O. The absorption peaks of 1261, 844, and 804 cm⁻¹ are assigned to the symmetric stretching of SiMe₃ (x = 1, 2, or 3), the stretching and/or rocking of SiMe₄, and SiMe₅ bonds, respectively. The largest peak of 1029 cm⁻¹ corresponds to the asymmetric stretching of Si-O-Si bonds. The enlargement for each SiMe₃ peak is shown in Fig. 1b for clarity. The SiMe₃ peak intensity appears to decrease after the annealing in N₂ ambient (N), but it should be noted that the comparison among the spectra is meaningful only when thickness correction is performed according to Beer's law. Meanwhile, annealing has decreased the thickness of all the samples by 4%. The thickness loss during annealing has been reported among other low-k materials and it is associated with the removal of the porogen co-deposited in the films. The SiMe₃ and Si-O-Si peak intensities before and after the correction are plotted in Fig. 1c. The FTIR spectra of water absorption ranging from 1400 to 2000 cm⁻¹ are depicted in Fig. 1d. The as-deposited sample shows some water absorption because of the room temperature deposition, but N sample has almost no water absorption. It is certain that the intensity and position of the SiMe₃ peak show negligible changes after the N₂ ambient annealing, indicating that the annealing in an inert ambient does not affect the methyl groups that directly bond to Si atoms. The Si-O-Si peak intensity of sample N is higher than that of the as-deposited sample; it is attributable to the dehydration and condensation reactions that thermal energy created. After the hydrogen-added annealing (F₁ and F₂), however, three methyl-related peak intensities slightly decrease, as shown in Fig. 1a-c; the intensities are larger than that of sample O, but smaller than that of sample N. In addition, it can be confirmed in Fig. 1d that noticeable water absorption exists in samples F₁ and F₂.

The relatively large number of methyl groups decreases...
during annealing in oxygen ambient. Note that, as shown in Fig. 1b, sample O presents smaller intensity at lower wavenumber of 1270–1240 cm\(^{-1}\) compared to the other four samples. As Ross et al. has reported, main building blocks of a-SiOC:H materials are “M (SiMe\(_3\), 1250 cm\(^{-1}\)),” “D (SiMe\(_2\), 1260 cm\(^{-1}\)),” “T (SiMe\(_1\), 1270 cm\(^{-1}\))” and “Q (SiO\(_2\))” groups.\(^{14}\) The relatively small peak intensity at lower wavenumber suggests that some of “M,” “D,” and/or “T” groups changed into “Q” and/or -OH bonded to Si atoms. As a result, the amount of carbon in the film decreased after oxygen ambient annealing. In addition, due to its highly oxidative nature, methyl-deprived Si atoms appear to bond with adjacent oxygen atoms, resulting in a large increase in the Si-O-Si peak intensity, as shown in Fig. 1a and c. Table I summarizes the FTIR result and additional experimental data that will be discussed below.

![Figure 1](image)

Figure 1. (a) The FTIR spectra of the as-deposited sample and samples N, F1, F2, and O. (b) Each SiMe\(_x\) peak is enlarged for clarity. (c) Intensities of the SiMe\(_x\) (squares) and Si-O-Si (triangles) peaks before (closed) and after (open) the thickness correction. (d) FTIR spectra of water absorption ranging 1400 to 2000 cm\(^{-1}\).

To indirectly verify the effect of micro-pore generation on lowering dielectric constant, TDS measurements were performed on the as-deposited sample and sample N. Figure 2b presents the TDS spectra of CH\(_3^+\) (m/z = 15), CH\(_3\)CH\(_2^+\) (m/z = 43), and COH\(_3^+\) (m/z = 31) ions of the as-deposited sample (solid lines) and sample N (dotted lines). The above-mentioned three ions were the ones with the highest ion currents. The out-gassing behaviors of those three ions bear a similarity from room temperature to 550°C. At low temperature region from room temperature to 200°C, three ions of the sample N show high ion currents relative to the as-deposited sample. It may be attributed to adventitious hydrocarbons that adsorbed on the film surface after the annealing; Auger electron spectroscopy (AES) depth profile data confirmed that the carbon concentration near the surface of annealed sample is higher than that of as-deposited sample (data not shown). At high temperature region from 200 to 550°C, however, ion currents of the as-deposited sample are higher than those of the annealed sample. To elaborate on the result, volatile hydrocarbons incorporated in the film easily evaporate from the film surface at high temperature.

<table>
<thead>
<tr>
<th>Samples</th>
<th>SiMe(_x)/Si-O-Si (%)</th>
<th>Dielectric constant (k)</th>
<th>Water contact angle (°)</th>
<th>XPS Si-OH proportion (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>As-deposited</td>
<td>31.1</td>
<td>3.58</td>
<td>69.2</td>
<td>6.2</td>
</tr>
<tr>
<td>Sample N</td>
<td>28.2</td>
<td>2.36</td>
<td>97.6</td>
<td>3.7</td>
</tr>
<tr>
<td>Sample F1</td>
<td>27.2</td>
<td>2.40</td>
<td>95.5</td>
<td>5.1</td>
</tr>
<tr>
<td>Sample F2</td>
<td>27.2</td>
<td>2.55</td>
<td>89.9</td>
<td>10.9</td>
</tr>
<tr>
<td>Sample O</td>
<td>23.6</td>
<td>3.70</td>
<td>64.0</td>
<td>10.2</td>
</tr>
</tbody>
</table>

Table I. The intensity ratio of SiMe\(_x\) to Si-O-Si, dielectric constant, water contact angle, and XPS Si-OH proportion of a-SiOC:H low-\(k\) films under different annealing conditions.
analyses presented above reveal that annealing in an N₂ ambient vapor pressure requirement of 400°C. Consequently, the FTIR and TDS spectra of ion currents at 550°C indicate that radical decomposition of the samples groups that bonded with Si atoms.

The dielectric constants of the hydrogen ambient annealing samples (F1 and F2) are higher than that of sample N. The dielectric constant increases from 2.36 to 2.40 and 2.55 as the hydrogen amount added in an N₂ annealing ambient increases from 0% (N) to 5% (F1) and 10% (F2). As shown in Fig. 3a, the C-V traces for samples N, F1, and F2 make it clear that both samples F1 and F2 have hysteresis of 0.6 V whereas sample N’s hysteresis is 0.3 V. The large hysteresis is highly likely the result of the polar characteristics of moisture molecules that adsorbed on both samples F1 and F2. The increases in the peak intensity of water-related species as shown in Fig. 1d supports the deliberation. Although hydrogen–added annealing slightly increases the dielectric constant, the values obtained is higher than that of the intact as-deposited sample and lower than that of the reported ashing process. The increase of the dielectric constant relative to the as-deposited sample may be attributed to the thermal energy of the annealing. Drastic increases in water contact angle of sample N denotes that annealing at 450°C desorbs the water-related species. It also indicates that the film surface becomes more hydrophobic, which is consistent with a disappearance of the water-related peak identified with hydroxyl groups in Fig. 1d. The addition of H₂ in annealing ambient makes the film surface less hydrophobic than sample N; the contact angle decreases from 97.6° to 95.5° and 89.9°, which is also consistent with FTIR spectra as shown in Fig. 1d. A subsequent adsorption of ambient water molecules may be activated through polar groups of Si-H and/or Si-OH located near the film surface. The removal of methyl groups and corresponding increase of Si-O bonds greatly decreases the contact angle of sample O.

The XPS curve-fitting of the Si 2p core level was performed to analyze chemical bonding states of main building blocks of each film. It indicated that as the annealing conditions varies from as-deposited sample to samples N, F1, F2, and O, “Q” group proportion decreases while “O” group proportion increases. This is consistent with the reduction of methyl groups as previously discussed in the FTIR spectra of Fig. 1d. The Si-OH proportion, however, shows no tendency that we have previously discussed. We speculate that the small increase in the proportion of -OH which replaces oxygen atoms has little impact on the binding energy change of Si atoms within experimental errors. We focused on the O 1s core level instead, since -OH groups have a direct impact on the binding energy of oxygen atoms.

Figure 4a illustrates the XPS curve-fitting of the O 1s core level
ent annealing has more Si-O bonding, which is hydrophilic in nature. The annealing condition of F2 and O showed a drastic deviation of Si-OH proportion between samples F1 and F2 may be explained as follows. Existence of more -OH bonds in sample F2 highly activates the water molecules result in an additional adsorption of the molecules. The Si-OH proportion of sample O is 10.2% which is smaller than that of sample F2. The annealing condition of F2 and O showed similar Si-OH group level by XPS, but sample O exhibited a larger decrease in water contact angle. The film that experienced O ambient annealing has more Si-O bonding, which is hydrophilic in nature, and less Si-CH3 bonding compared to sample F2. Compared to the Si-O bond, -OH related groups’ relative ability to decrease the water contact angle is negligible.

We deposited a-SiOxCH film with the lowest k value of 2.36 and investigated how the electrical and structural properties of the deposited films change depending on annealing conditions. The annealing in an inert N2 ambient does not affect the methyl groups that directly bond to Si atoms, while it removes weakly bonded organic fractions without any harmful effects on the film, resulting in a large decrease in dielectric constant. The dielectric constant of the film becomes larger than that of the as-deposited sample after oxygen ambient annealing. We showed that a small amount of hydrogen mixed in N2 changes the film surface more hydrophilic, which is favorable to the surface cleaning process without causing large loss of carbon and resultant large increase of dielectric constant. We propose that a small amount of hydrogen-adde...