Effect of Surface Treatments on the Electrical Properties of Fluorinated Silicon Oxides

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In this study, different surface treatments of HF-based etching solutions are investigated for the predeposition of liquid-phase deposited fluorinated silicon oxides (LPD-SiOF). The effects of each etching solution on the interface trap density and breakdown field are examined with Al/LPD-SiOF/Si structure. From the experimental results, there appears significant growth delay time for different surface treatments during the initial oxide deposition, which is defined as the surface modification time to reach an OH-rich surface promoting the growth of LPD-SiOF film. However, the subsequent deposition rate remains unchanged for all etching processes, indicating a surface-independent deposition process. It is found that a two-step treatment in dilute HF/H₂O with 1:200 v/v ratio reveals an average breakdown field of 9.7 MV/cm and an extremely low average interface trap density (~10¹⁰ eV⁻¹ cm⁻²), which are comparable to that of thermal oxides. Moreover, the rapid thermal annealing process is suggested to clearly improve the oxide quality for this two-step etching process, where early breakdown is eliminated (18% raising for EBD) and interface properties are substantially improved (33% reduction for DIT). The improvements for device performances are believed to be due to the oxide-free Si surface passivated with hydrogen and reduced surface microroughness (Rₐ = 0.1 nm). It is evident from our experiments that this new two-step surface treatment is an effective method for interface improvement with oxide deposited by LPD or chemical vapor deposition.

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In the integrated circuit (IC) fabricating process, a suitable surface treatment in addition to standard RCA cleaning is required to completely remove contaminants of organic materials or metallic ions contained in the native oxide and reduce surface microroughness. It is well known that surface microroughness at the SiO₂-Si interface has a significant effect on the electrical properties of metal-oxide-semiconductor (MOS) devices as gate oxide scales down to nanometer size. A silicon surface with no native oxide and full hydrogen-passivated surface is an important issue to be assured of high breakdown field, high charge to breakdown, and low leakage current. In the literature, a promising dry cleaning technology of plasma etching was shown to remove oxygen from the Si surface effectively, as well as improve charge to breakdown; however, the Si surface was roughened with plasma-damaged lattices. Other newly developed dry cleanings, including laser cleaning for the removal of surface particles, gas-phase surface cleaning using anhydrous HF/methanol, UV/C₁₂, and UV/O₂ in situ cleaning in a hydrogen ambient at atmospheric pressure using HF and HCl gas, and Cl radicals generated with UV irradiation, were investigated. These dry cleaning methods showed effective removal of submicron particles, native oxides, and Fe contaminants. Nevertheless, dry cleaning showed inferior performance, for example, for Ca removal and surface microroughness, in comparison with wet cleaning. As an alternative, a convenient method of cleaning technology based on H₂O₂ chemistry in semiconductor manufacturing processes of high temperature thermal annealing to densify the oxide films. A high temperature thermal annealing, such as N₂ furnace annealing, rapid thermal oxidation (RTO), O₂ and H₂ plasma, and rapid thermal nitridation (RTN) tends to alter the oxide bonding characteristics, leading to a denser oxide network and/or strengthening of Si-O bonds near the oxide-Si interface by reducing oxygen vacancies. Therefore RTA is also employed in this study to drive fluorine out of LPD oxides and densify LPD-SiOF films since this is an effective and rapid annealing for future ultralarge scale integrations (ULSIs). It was found that oxide breakdown field and interface properties were clearly improved.

Experimental

n-Type silicon wafers with (100) orientation and resistivity of 9-12 Ω-cm were used as the substrates. For RCA cleaning, substrates were boiled in an APM solution (NH₄OH/H₂O₂/H₂O) with a volume ratio of 0.05:10:50 at 80°C for 15 min to remove organic materials on the started substrates. The smaller content (i.e., 0.05) of NH₄OH other than that (i.e., 10) in conventional RCA cleaning has been demonstrated to greatly reduce the surface microroughness. After dipping APM-treated substrates into ultraclean DI water for 5 min, they were subjected to HPM solution (HCl/H₂O₂/H₂O) with a volume ratio of 10:10:60 at 80°C for 15 min to remove alkaline ions and metallic ions. These substrates with chemically formed native oxides

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A detailed and complete oxide growth mechanism was suggested in relation to surface treatments since interface properties are strongly dependent on surface morphology. Oxide quality improvements including breakdown field and average interface trap density after various surface treatments were investigated. Moreover, it has been widely used in semiconductor manufacturing processes of high temperature thermal annealing to densify the oxide films. A high temperature thermal annealing, such as N₂ furnace annealing, rapid thermal oxidation (RTO), O₂ and H₂ plasma, and rapid thermal nitridation (RTN) tends to alter the oxide bonding characteristics, leading to a denser oxide network and/or strengthening of Si-O bonds near the oxide-Si interface by reducing oxygen vacancies. Therefore RTA is also employed in this study to drive fluorine out of LPD oxides and densify LPD-SiOF films since this is an effective and rapid annealing for future ultralarge scale integrations (ULSIs). It was found that oxide breakdown field and interface properties were clearly improved.

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In this paper, the effects of various surface treatments (or cleaning processes) are investigated in relation to surface treatments since interface properties are strongly dependent on surface morphology. Oxide quality improvements including breakdown field and average interface trap density after various surface treatments were investigated. Moreover, it has been widely used in semiconductor manufacturing processes of high temperature thermal annealing to densify the oxide films. A high temperature thermal annealing, such as N₂ furnace annealing, rapid thermal oxidation (RTO), O₂ and H₂ plasma, and rapid thermal nitridation (RTN) tends to alter the oxide bonding characteristics, leading to a denser oxide network and/or strengthening of Si-O bonds near the oxide-Si interface by reducing oxygen vacancies. Therefore RTA is also employed in this study to drive fluorine out of LPD oxides and densify LPD-SiOF films since this is an effective and rapid annealing for future ultralarge scale integrations (ULSIs). It was found that oxide breakdown field and interface properties were clearly improved.

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Table I. The six surface cleanings used in this study are detailed and complete parameters for different cleanings are given.

<table>
<thead>
<tr>
<th>Sample</th>
<th>RCA concentration</th>
<th>HF:MeOH:H₂O₂:DI (min)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CN-1</td>
<td>RCA:HF:MeOH:H₂O₂</td>
<td>1:40:10:60:30</td>
</tr>
<tr>
<td>CN-3A</td>
<td>RCA:HF:MeOH:H₂O₂</td>
<td>1:10:200:30</td>
</tr>
<tr>
<td>CN-3B</td>
<td>RCA:HF:MeOH:H₂O₂</td>
<td>1:10:30:200</td>
</tr>
<tr>
<td>CN-4B</td>
<td>RCA:HF:MeOH:H₂O₂</td>
<td>1:200:5.0:5.0:50</td>
</tr>
<tr>
<td>CN-5B</td>
<td>RCA:HF:MeOH:H₂O₂</td>
<td>1:200:10:5.0</td>
</tr>
<tr>
<td>CN-6B</td>
<td>RCA:HF:MeOH:H₂O₂</td>
<td>1:200:10:5.0</td>
</tr>
</tbody>
</table>

These etching processes right after the RCA cleaning process tended to modify surface properties remarkably. This can be explained by first noting the growth curves. As shown in Fig. 1 for the typical characteristics of oxide thickness vs. deposition time, obvious growth delay time (GDT) appears during the initial growth. The GDT for CN-1 is shorter (0 min, not shown in this figure) than CN-4B because CN-1 receives a 5 min DI water rinse. Owing to the growth of native oxide, no GDT is observed. GDT is estimated to be within 12 min when a two-step etching process (CN-4B) is used. For the same reason, CN-3B shows shorter GDT (2 min, not shown in this figure) than CN-3A because of the DI water rinse. Interestingly, no GDT is seen in CN-5B, which is believed to be due to the growth of native oxide during the etching process by the oxidized reaction of HNO₃ and Si. On the contrary, CN-6B used H₂O₂ instead of H₂O to suppress the autocatalytic reaction of HNO₃ with Si, hence little native oxide was obtained (GDT = 5 min, not shown in this figure). Furthermore, chemical oxides formed by HNO₃ were etched off completely by HF because the rate-determining step was the oxidation of Si by HNO₃. After the growth of the first atomic layer of LPD-SiOF, the deposition rate was almost the same, no matter which etching process was treated on Si substrate (i.e., surface-independent growth mechanism for LPD). It is therefore suggested that some surface modifications occur during the growth of LPD-SiOF for various surface treatments.

Initial LPD growth mechanism.—The explanations for GDT can be understood from the growth mechanism. Initially, the RCA-treated Si surface is full of chemically formed native oxide. Subsequent dipping in HF-based etching solutions with primary species of integral HF molecule leads to the fact that these molecules can easily insert themselves between Si and O of Si-O bond and leave Si-F bonds on the sample surface. The polar nature of the Si-F bond makes it susceptible to HF attack, which frees the SiF₆³⁻ species into the solution and simultaneously forms hydrogen termination. HF-treated Si(100) surface will therefore be covered mainly by Si-H and Si-H₂ bonds. The hydrogen on the Si surface will be replaced by hydroxyl through the reaction of Si-H + H₂O → Si-OH + H₂ which is favorable for the growth of LPD-SiOF. The necessity of Si-OH bonds on the substrate surface and formation of intermediate species in the LPD growth solution are common features because the intermediate polysilic acid is formed by the polymerization of silic monomer Si(OH)₄ where two different intermediate species, SiF₆⁵⁻(OH)₄₋ₙ and (SiF₆⁻SiF₄)²⁻, have been proposed. F atoms

![Figure 1. Typical growth curves of oxide thickness vs. deposition time. It is revealed that different surface etching processes lead to substantial variations of growth delay time (GDT).](http://example.com/image.png)
of intermediate species react with Si-OH bonds and form the first monolayer of LPD-SiOF and the residual intermediate species can then easily react with existing LPD-SiOF film by the bonding reaction of
\[ \text{SiF}_m(\text{OH})_{4-m} + \text{SiF}_n(\text{OH})_{4-n} \rightarrow \text{SiF}_{n+m} \text{H}_{4-n} \text{SiF}_{n-m}(\text{OH})_{4-n} + \text{HF} \]

It is evident that GDT is present during the growth of LPD-SiOF, which is shown to be due to the native oxide-free surface. The deposition rate depends only on the reaction mechanism in the growth solution; that is, surface pretreatment shows no effect on the subsequent oxide growth. We have a preliminary result that surface treatment mainly affects the interface bonding configurations for LPD oxides and perhaps some leakage current paths caused by surface roughness are also taken into consideration. In the following discussions, effects of various surface treatments are shown and compared on the basis of breakdown fields and interface properties.

**Distribution of oxide breakdown field.**—In this section, results for breakdown field of MOS capacitors with Si substrates treated by various etching steps are illustrated in Fig. 2, where Fig. 2a shows oxide failure percentage for as-deposited LPD-SiOF and Fig. 2b shows oxide failure percentage after RTA. The range of the breakdown field is found between 3 and 11 MV/cm. This figure indicates an extrinsic breakdown which is due to impurity related reduction of effective oxide thickness. The incorporated fluorine atoms in the LPD oxide were considered to be the origin of impurity traps, which are evidently positive charges by high frequency C-V measurement that flatband voltage shifts to more negative axis. Oxide quality of breakdown endurance can also be improved by RTA treatment, as shown in Fig. 2b. After high temperature annealing for LPD-SiOF, the breakdown field increases to higher than 10 MV/cm on average. Some breakdown fields for RTA-treated LPD-SiOF can be even higher than 15 MV/cm. This high breakdown field is superior to that of plasma etching (4.4-9.6 MV/cm).\(^5\) The improvement of oxide breakdown field after RTA is believed to be due to F driven out of LPD-SiOF film and hence the oxide bonding network rearranges to a denser structure. RTA is also supposed to change the bonding characteristics near the oxide-Si interface by reducing nonbridging oxygen centers and unbonded Si-O bonds, which are more evident and discussed in detail in the next section. It is therefore concluded that a high-temperature annealing obviously promotes the oxide quality to an intrinsic breakdown behavior.

**Average interface trap density.**—In order to examine the changes of the Si-SiO\(_2\) interface, the average interface trap density for both as-deposited and RTA LPD-SiOF were measured from C-V curves, which are shown in Fig. 3. Moreover, the average breakdown fields for various treatment processes are also calculated to check the improvement shown in this study. It can be seen that sample CN-4B shows the lowest average interface trap density and highest average breakdown field for both as-deposited and RTA ones. Compared to CN-1, CN-4B was under a two-step etching process with heavily diluted HF concentration and longer etching time (refer to Table I). It has been found that full passivation of the Si surface (hence the contact angle is larger than 70\(^ {\circ} \)) can be reached by the length of time of the HF dip.\(^3,4\) In this study, a volume ratio of 1:200 for HF/H\(_2\)O was used in order to slow down the etching rate so that surface microroughness was reduced. On the other hand, after a DI water rinse, partial reoxidation of the Si surface is reached and the contact angle is also decreased. It is important to note that only when full passivation of hydrogen is obtained, no reoxidation occurs during the DI water rinse while a small number of particles is observed after rinsing and drying. We found that CN-4B can meet the requirements described in the above.

In the case of RTA, average interface trap density was lowered to an order of less than 5 \( \times 10^{10} \) eV\(^{-1}\) cm\(^{-2}\). This value is much smaller than that (2-3 \( \times 10^{11} \) eV\(^{-1}\) cm\(^{-2}\)) in the plasma etching of CF\(_3\)/H\(_2\) gas mixture.\(^4\) It is speculated that plasma etching produces the following damage: residue and surface film formation, contamination from etching species, and lattice damages, which will greatly influence the interface behavior of MOS devices.\(^5\) It is interesting to note that average breakdown fields for all treatments after RTA were in the range of 10 to 11 MV/cm. We attempt to show the improve-

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**Figure 2.** Breakdown field distribution of 10 nm as-deposited LPD-SiOF (a) and RTA LPD-SiOF (b) for six etching solutions utilized in this study. The extrinsic breakdown (3-8 MV/cm) is ascribed to the fluorine atoms induced positive charges acting as electron traps.

**Figure 3.** Average breakdown field and average interface trap density for six treatments. CN-4B shows the lowest average interface trap density and highest average breakdown field, which is ascribed to full hydrogen-passivated surface and reduced surface microroughness (see Fig. 5). After the RTA process, all samples were increased to a sufficiently high breakdown field (10-11 MV/cm).
oment of the average breakdown field being ascribed to the densification of oxide film. The bonding strength of the Si-SiO	extsubscript{2} interface was determined by whether a completely hydrogen passivated surface was reached or not. According to the growth mechanism in the LPD system described in the section on the Initial LPD growth mechanism, a replacement of Si-H by Si-OH is beneficial for intermediate species in the growth solution to bond with OH on the Si surface. Lower average interface trap density of CN-3A to CN-6B than control one is a result of a high degree of hydrogen passivation.

Among these six treatments, both CN-1 and CN-3B received a DI water rinse before drying. In the literature, it has been reported that the reaction of H	extsubscript{2}O with the HF-treated Si surface obviously shows the appearance of surface OH groups

\[
\text{Si-F + H-OH} \rightarrow \text{Si-OH} + \text{HF}
\]

followed by a rupture of Si-Si bonds and finally the formation of Si-O-Si bridges\textsuperscript{35}

\[
\text{Si-OH} + \text{Si-OH} \rightarrow \text{Si-O-Si} + \text{H}_{2}\text{O}
\]

It was believed that eliminating water in the final step of treatment is preferable in the consideration of leakage current and charge to breakdown for thermal oxides. In Fig. 3, the breakdown field of as-deposited CN-3B is a little smaller than CN-3A where no DI water rinse was done. It is interesting to find that the average interface trap density of the DI water rinsed sample is reduced compared to that without the DI water rinse. It is suspected to be a further modification of HF in the growth solution, as can be seen in the LPD reaction process

\[
\text{H}_2\text{SiF}_6 + 2\text{H}_2\text{O} \rightarrow \text{SiO}_2 + 6\text{HF}
\]

This will change the Si surface to be covered with full Si-H bonds. Nevertheless, in the next three etching processes (CN-4B, CN-5B, and CN-6B), no DI water rinse was used.

Comparing both SE (CN-5B) and CSE (CN-6B) with dilute HF (CN-4B), a great difference of average breakdown field and average interface trap density is obtained. The CSE solution has been found to reduce the surface concentrations of Fe and Cu ions and to suppress the average surface microroughness increase in comparison with SE solution. The SE cleaning process is not so effective as dilute HF and CSE because HNO\textsubscript{3} will oxidize Si surface. In the previous report,\textsuperscript{5} SE slightly dissolves the Si surface and the microroughness becomes worse while the CSE etches native oxide. Meanwhile, the average breakdown field for SE was 8.1 and 11.5 MV/cm for CSE. In comparison, our LPD-SiOF deposited on CSE-treated surface shows comparable breakdown field (10 MV/cm) as thermally oxidized surface for as-deposited and RTA one. The average interface trap density was as low as $6 \times 10^{10}$ eV\textsuperscript{-1} cm\textsuperscript{-2}. The evident increase of the average breakdown field and decrease of average interface trap density by RTA are clearly seen.

**Surface microroughness for various treatments.**—Since surface microroughness has a severe influence on thin oxide quality, the best treatment is shown by surface image of the six treatments. Figure 4 illustrates the atomic force microscopy (AFM) surface images for six surface-cleaned Si substrates. The scanning area of each substrate is $2 \times 2$ $\mu$m. These pictures indicate that the surfaces are lumpy, especially for CN-1, 3B, and 6B. Some black features are found, and they may be particles due to environmental contaminations. Figure 5 gives the mean microroughness ($R_a$) for the Si surface treated with six etching solutions. $R_a$ for CN-4B is 0.1 nm and that for CN-5B is 0.761 nm. In the literature,\textsuperscript{4,36,37} it has been confirmed that the increase of surface microroughness would severely degrade the breakdown characteristics ($E_{BD}$ and $Q_{BD}$) of a thin oxide with a thickness of 8 nm and below. This is due to effective oxide thickness reduction, which means that some areas of extremely thin oxides exist and the current can flow through these tunneling paths easily. In comparison with the breakdown field in Fig. 3, it is evident that the $E_{BD}$ is in direct relationship with $R_a$, with the exception of CN-1. From CN-1 and CN-4B, it is further concluded that a long-time etch with greatly diluted HF/H\textsubscript{2}O solution could effectively reduce the surface microroughness. The AFM image of CN-5B contains many grains, due to the oxidation of Si by HNO\textsubscript{3} during the surface etching process. CN-6B shows reduced $R_a$ because H\textsubscript{2}O\textsubscript{2} suppresses the autocatalytic reaction of HNO\textsubscript{3} and Si. The surface microroughnesses in this study are found to be comparable to other etching processes with microroughness of 0.1-1 nm.\textsuperscript{14-18}

**Conclusions**

Six different etching solutions, including dilute HF, methanol/HF, HNO\textsubscript{3}/HF/H\textsubscript{2}O, and HNO\textsubscript{3}/HF/H\textsubscript{2}O\textsubscript{2}, were used as surface treatment processes right after the standard RCA cleaning. These surface etching steps lead to a large variation of the degree of hy-
Breakdown fields were demonstrated to be related to surface microroughness of various etching processes. A two-step etching process shows the lowest microroughness of 0.1 nm.

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