Properties and reliability of ultrathin oxides grown on four inch diameter silicon wafers by microwave plasma afterglow oxidation

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We have successfully grown ultrathin oxides on large area of silicon wafers by the microwave plasma afterglow oxidation method. Analysis of the Fourier transform infrared spectra indicates that the general bonding structures of the ultrathin oxides grown by microwave plasma afterglow oxidation at 700 °C could be identical to those grown by dry O2 thermal oxidation. Electrical property measurements (e.g., time-zero dielectric breakdown and time-dependent dielectric breakdown) are also investigated. Based on our results, we conclude that microwave plasma afterglow oxidation is a useful method for the preparation of large area ultrathin oxide films on silicon substrates. © 1998 American Vacuum Society. [S0734-211X(98)04405-9]

I. INTRODUCTION

The miniaturization of metal–oxide–semiconductor field effect transistor (MOSFET) devices has been progressing rapidly in recent years. The advance of ultralarge scale integrated (ULSI) devices has led to the need for thinner oxide films. The thickness of the dielectric films for 0.2 μm feature size MOSFETs is 6.5 nm.1 As the feature size goes down to 0.09 μm, the thickness of the gate oxide is 4 nm, limited by direct tunneling through the oxide. The properties and reliability of these dielectrics become more critical than in thicker dielectrics. Low defects and low interface state concentrations, free from planar stress, and high breakdown strength are indispensable characteristics for ultrathin dielectrics in deep submicron devices. Typical requirements for the electrical properties of ultrathin oxides in commercial devices include a breakdown field $E_{bd} \geq 7$–8 MV/cm and interface densities $D_{it} \leq 5 \times 10^{10}$ cm$^{-2}$ eV$^{-1}$.2 How to meet these requirements is a big challenge for future ULSI development.

Following conventional thermal oxidation, high-temperature annealing is the best way to reduce defects and interface states. However, in the ULSI regime, high temperatures (≥900 °C) will induce impurity diffusion and cause dopant redistribution. Therefore, low-temperature (≥800 °C) processing becomes desirable to maintain shallow dopant profiles as device dimensions shrink. There are two important approaches to satisfy the low thermal-budget requirements. One of them involves utilization of the plasma-assisted technique for depositing or growing thin films at low temperatures, which includes electron cyclotron resonance (ECR) plasma oxidation,3,4 remote plasma-enhanced chemical vapor deposition (RPECVD),5,6 and microwave plasma afterglow oxidation.7–10 The other is the rapid thermal process (RTA) in which samples are heated by intense light.11–13

Microwave plasma afterglow oxidation is a low-temperature, microwave-induced-plasma-assisted oxidation process. Oxygen flows into the resonance cavity and is ionized by hot electrons coupled to the additional energy provided by the microwaves. There are many excited atomic oxygen species and hot electrons generated by this process.

Microwave plasma afterglow oxidation has a reduced thermal budget and it can grow good quality oxides.7–10 Microwave afterglow plasma oxidation is a potential technique for future ULSI device fabrication. According to our previous studies,7–10 ultrathin oxides grown at 600 °C on 2 × 2 cm$^2$ substrates by the microwave afterglow plasma oxidation method using N$_2$O plasma annealing and pretreatment, followed by 900 °C RTA processing, show a breakdown field of 12 MV/cm and reduced the density of states in the middle of band gap of 5 × 10$^{10}$ cm$^{-2}$ eV$^{-1}$. It is, therefore, interesting to see if this method could be extended to grow ultrathin oxides on large diameter wafers.

II. EXPERIMENT

The schematic diagram of the microwave plasma afterglow oxidation system consists of four parts, pumping system, high-temperature furnace, gas sources, and microwave plasma generation system. The system is equipped with N$_2$, O$_2$, Ar, N$_2$O, and HCl gases, which flow into the system from the back end of the furnace and enter the discharge regime to form the excited plasma. Plasma flows through the reaction regime and is pumped out from the front end of the furnace. The gas pressure is monitored by a MKS Baratron gauge. To prevent the energetic particles directly damaging samples, the samples were placed approximately 25 cm away from the plasma glow discharge region.

MOS capacitors were fabricated for electrical property studies. 4 in., N-type, 3.5–4.5 Ω cm, (100)-oriented Si wafers were used as the substrates. Field oxide layers with a thickness of 500 nm were thermally grown by wet oxidation. These wafers were then patterned and etched to form square holes with different sizes in the capacitor regions where the ultrathin oxides were grown later. After the ultrathin oxides...
were grown, the samples were coated with an aluminum layer by electron-beam evaporation. For making electrodes on the substrates, aluminum film was deposited on the back-side of these samples. 400 °C post-metallization annealing (PMA) process was carried out in pure N₂ ambient. Samples were cleaned by a modified RCA method prior to the oxidation process. The cleaning steps include (i) boiling in a solution of H₂SO₄(98%):H₂O₂(30%)=1:10 at 120 °C for 10 min, (ii) dipping in a solution of HF(49%):DI water =1:10 for about 10 s, (iii) boiling in a solution of NH₄OH(27%):H₂O₂(30%):DI water=25:1:5 at 80 °C for 10 min, (iv) dipping in a solution of HF(49%):DI water =1:10 for about 10 s, (v) boiling in a solution of HCl(37%):H₂O₂(30%):DI water=1:1:6 at 80 °C for 10 min, (vi) dipping in a solution of HF(49%):DI water=1:10 for about 10 s. Each step was followed by a DI water rinse before transferring into the next solution.

Ultrathin oxides were grown at 700 °C in 100 sccm and 150 sccm O₂ with Ar mixture and the microwave power was set at 500 W. The total operation pressure was 6.57 Torr for oxide film thickness controlling runs and 8.4 Torr for the capacitor fabrication. Before the oxidation took place, all wafers were cleaned by the modified RCA method and dipped in HF solution to make sure no native oxides left on the silicon surface.

By optimizing the growth conditions, such as pressures, temperatures, gas flow rates, and growth time, the thickness uniformity can be improved. Thickness of the ultrathin oxides were determined by ellipsometry and C–V measurements. High resolution transmission electron microscopy (HRTEM) was used to calibrate the results of ellipsometry and C–V measurements. As the thickness uniformity was well controlled, Fourier transform infrared (FTIR) analysis was employed to identify the Si–O bonding of ultrathin oxides. At the same time, capacitors were fabricated for investigating the electrical properties of ultrathin oxides by utilizing the I–V and C–V measurements.

### III. RESULTS AND DISCUSSION

#### A. Growth rate

The relationship between oxide thickness and oxidation time is shown in Fig. 1 which shows that there are two stages of growth. The same phenomenon was observed previously. In the first stage, the thickness increased at a growth rate of 0.216 nm/min. As the thickness reached 4.5–5 nm, the growth rate became 0.050 nm/min. The two different growth rates show that the excited oxygen species react rap-
idly with the silicon surface, and after the surface is covered by SiO₂, the oxygen atoms diffuse through the oxide layer and react with the underlying silicon substrates. Then the reaction rate decreases to a lower value.

According to the growth rate of the first stage, the thickness below 4.5–5 nm is difficult to control. However, it could be controlled by reducing the oxygen gas flow rate.

The oxide thickness decreased along the longitudinal direction, this phenomenon is similar to that predicted by Chou’s model. Furthermore, as the microwave power increased, the oxide thickness was found to be increased as shown in Fig. 2. By increasing the microwave power, the energy coupled to the oxygen atoms is increased, and both the concentration of excited oxygen species and growth rate are increased.

B. Thickness uniformity control

Microwave plasma afterglow oxidation has been proved to be able to fabricate good quality ultrathin oxides. However, its applicability to large area wafers has not yet been demonstrated. In this study, it was found that the uniformity could be controlled within 5% of the deviation. However, it strongly depended on the operation conditions, including the pressure gas flow rates, gas flow patterns, and the arrangement of the wafers. As depicted in Fig. 3 and Table I, the tilt arrangement of the wafer was found to improve the thickness uniformity.

C. Some fundamental properties

1. Physical properties

Figure 4 shows the FTIR spectra of the O₂ plasma as-grown ultrathin oxide, thermally grown dry oxide and wet oxide. The FTIR peak position of the Si–O stretching mode of the oxide grown by microwave plasma afterglow oxidation is 1073.8 cm⁻¹. It is near the peak position of oxide grown by dry oxidation. The peak position of the O₂ plasma as-grown ultrathin oxide prepared by our previous 4 cm² wafer system at 600 °C is 1058 cm⁻¹. According to the publication, the FTIR peak position of the Si–O stretching
mode is around 1075 cm\(^{-1}\) and the peak position shifts from lower wave number to higher wave number as the oxide film becomes thicker.\(^{18,19}\) It is because the oxide structure gets denser.

The ultrathin oxides grown with different microwave powers showed the FTIR peak position of the Si–O stretching mode at around 1073 cm\(^{-1}\) and it was power independent. The dielectric constant and refractive index of the ultrathin oxides grown by the microwave plasma afterglow oxidation method were also determined to be 3.25 and 1.465, respectively. The well accepted values for the two constants are 3.9 and 1.46, respectively.

2. Electrical properties

The effective oxide charge density can be derived from the quasistatic frequency \(C-V\) and high frequency \(C-V\) measurements. Figure 5 shows the \(C-V\) plots of capacitors with thickness of 6, 8, 10 nm as-grown oxide layers grown by the microwave plasma afterglow oxidation method. The size of the capacitors is 4.84 \(\times 10^{-2}\) cm\(^2\). The measured thickness and the effective oxide charge densities are listed in Table II. The flatband voltages were found to range between \(-0.36\) and \(-0.50\) V and the effective oxide charge densities were found in the range of \(1 \times 10^{11} - 4 \times 10^{11}\) cm\(^{-2}\). However, the lowest value had ever been obtained was \(8.6 \times 10^{10}\) cm\(^{-2}\). In the same thickness range, the flatband voltages of the oxide grown by our original 4 cm\(^2\) wafer system were between \(-0.35\) and \(-0.37\) V and the effective oxide charge densities were \(5.8 \times 10^{10} - 8.8 \times 10^{10}\) cm\(^{-2}\).

3. Interface state density

The midgap interface state densities of the samples with 6, 8, and 10 nm thickness as-grown oxide layers grown by microwave plasma afterglow oxidation are also listed in Table II. The midgap interface state densities were between \(1 \times 10^{11}\) and \(3 \times 10^{11}\) cm\(^{-2}\) eV\(^{-1}\). The midgap interface state densities of the oxides grown by our original 4 cm\(^2\) wafer system were between \(4 \times 10^{11}\) and \(8 \times 10^{11}\) cm\(^{-2}\) eV\(^{-1}\). The lowest value obtained from the present measurement was \(7.53 \times 10^{10}\) cm\(^{-2}\) eV\(^{-1}\) as shown in Fig. 6. The results are

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**Table II. Properties of the ultrathin oxides grown by microwave plasma afterglow oxidation.**

<table>
<thead>
<tr>
<th>Sample description</th>
<th>Thickness (nm)</th>
<th>Flatband voltage (V)</th>
<th>Effective oxide charge (cm(^{-2}))</th>
<th>Midgap interface state density (cm(^{-2}) eV(^{-1}))</th>
<th>Breakdown (MV/cm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>700 °C, 500 W as-grown 10 min</td>
<td>6.2</td>
<td>-0.369</td>
<td>1.29(E)11</td>
<td>1.2(E)11</td>
<td>7.76</td>
</tr>
<tr>
<td>700 °C, 500 W as-grown 20 min</td>
<td>8.1</td>
<td>-0.406</td>
<td>1.96(E)11</td>
<td>2.04(E)11</td>
<td>8.21</td>
</tr>
<tr>
<td>700 °C, 500 W as-grown 30 min</td>
<td>9.5</td>
<td>-0.5</td>
<td>3.88(E)11</td>
<td>2.72(E)11</td>
<td>8.64</td>
</tr>
</tbody>
</table>

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**Fig. 6.** Interface state density \((D_{it})\) of the 6, 8, and 10 nm O\(_2\) plasma as-grown ultrathin oxide.
superior to the previous ones, and less interface state density of the oxide was obtained.

4. Reliability analysis

The time-zero dielectric breakdown characteristics curve of 8 nm O₂ plasma as-grown oxide is shown in Fig. 7. The histograms of the breakdown field distribution in capacitors with thickness of 6, 8, and 10 nm as-grown oxide layers prepared by microwave plasma afterglow oxidation are shown in Fig. 8. The size of the capacitors is 8.4 × 10⁻³ cm². Figure 9 shows the cumulative failure rate plots of the breakdown field in three samples with different oxide thickness. From these plots, the breakdown field was shown to distribute mainly from 7 to 9 MV/cm. The highest value of the breakdown field was found to be 9.5 MV/cm in the 8 nm thick oxide sample. The average breakdown field and its deviation are shown in Table III.

Time-dependent dielectric breakdown test was employed to investigate the breakdown characteristics of the ultrathin oxides. The various constant voltage stressings were applied to the capacitors with an area of 4.5 × 10⁻² cm². The relationship between the applied electric field and the time to breakdown of the 8 nm ultrathin oxide grown by microwave plasma afterglow oxidation is shown in Fig. 10. The larger the applied electric field was the shorter was the time needed to reach the breakdown. As the applied electric field reached 8 MV/cm, the time to breakdown was 2053 s.

The time to breakdown was measured with current stressing on the capacitor with 8 nm as-grown ultrathin oxide. Then the results were converted to the charge to breakdown and plotted as a function of various constant applied currents, as shown in Fig. 11. The value of the charge to breakdown was 9.1 C/cm².

The Fowler–Nordheim tunneling injected into the ultrathin oxide to evaluate reliability of the ultrathin oxides. The level of constant Fowler–Nordheim tunneling current used was 10 μA/cm² and the size of the capacitors was 4.84 × 10⁻⁴ cm². After Fowler–Nordheim tunneling current stressing, the shifts of flatband, the effective charge densities, and the midgap interface state densities were measured. The shifts of flatband voltage as a function of the stressing time (or the number of the injection electrons) are shown in Fig. 12(a). Figure 12(b) shows the effective oxide charge densities induced by Fowler–Nordheim tunneling electron injections. The shifts of midgap interface state density after the electron injections are shown in Fig. 12(c).

D. Improvements on the ultrathin oxides

It is generally known that the wafer surface cleaness is very crucial to the oxide quality. A recent publication showed that the properties of the oxide could be improved by
the RCA cleaning process with spin removal of the cleaning solution. We attempted to adopt ultrasonic vibration during the cleaning process to remove the cleaning solution more efficiently. The results showed that this technique could reduce both the effective charges and the interface state densities and also increase the breakdown fields. The modified RCA cleaning with ultrasonic vibration seems helpful to improve the oxide properties. The C–V curves and interface state densities were measured on as-grown oxides cleaned with or without ultrasonic vibration. The corresponding parameters are listed in Table IV.

In the past reports and our previous study, N₂O plasma annealing could increase the strength of the oxides. In this study, N₂O plasma annealing was also found to increase the oxide strength, but the effective oxide charge density and the interface state density were increased.

Another method adopted in this study was to use the N₂/O₂ plasma annealing. The N₂/O₂ gas ratio was 2/1. The thickness of ultrathin oxides increased after the annealing. The results showed that N₂/O₂ plasma reduced the effective oxide charges and interface state densities, but increased the oxide strength of the ultrathin oxide. However, the influence on the increasing thickness should be considered.

**Table III.** Average electrical breakdown and its deviation of the ultrathin oxides grown by microwave plasma afterglow oxidation.

<table>
<thead>
<tr>
<th>Average $E_{bd}$ (MV/cm)</th>
<th>Deviation</th>
</tr>
</thead>
<tbody>
<tr>
<td>700 °C, 500 W as-grown 10 min (6 nm)</td>
<td>7.81056</td>
</tr>
<tr>
<td>700 °C, 500 W as-grown 20 min (8 nm)</td>
<td>8.16187</td>
</tr>
<tr>
<td>700 °C, 500 W as-grown 30 min (10 nm)</td>
<td>8.41049</td>
</tr>
</tbody>
</table>

**Fig. 10.** Lifetime of the O₂ plasma as-grown ultrathin oxide during various electrical field.

**Fig. 11.** Charge to breakdown as function of Fowler–Nordheim tunneling stressing current.
In our previous study, fluorine pretreatment was considered to be a good method to increase the oxide strength. The fluorine was derived from dipping in HF for 10 s before the oxidation. The results showed that the breakdown fields were increased but the effective oxide charge and interface state densities were also increased.

In this study, slight HCl (about 2.5%) was added into the O₂ plasma during the oxidation. The results showed that the HCl-contained oxide possessed higher breakdown fields and fewer effective oxide charges. The mobile oxide charges might be reduced by the Cl₂ ions. However, the interface state densities were increased as HCl was added in the plasma oxidation process. The properties of the ultrathin oxides treated with the different improvement methods are compared in Table V.

From the FTIR spectra of the oxides annealed by N₂O plasma and N₂/O₂ plasma, and HF pretreated oxide, the peak positions of the Si–O stretching mode were all near 1074 cm⁻¹ and the peak of Si–N was not shown in the spectra. It might be due to that the nitrogen concentration was very low thus that the peak of Si–N bonding did not appear. Similar phenomena were observed in the N₂/O₂ annealed oxide and fluorine pretreated oxide.

IV. SUMMARY

Microwave plasma afterglow oxidation is an effective method to grow ultrathin silicon oxides at low temperatures by using chemically active atomic species. In the present study, such a system was set up to test the feasibility of this method for large area wafers. Uniformity of the ultrathin oxide could be controlled within 3%–5% under the appropriate conditions.

Growth rates of the ultrathin oxides were studied. The thickness of oxides decreased as the longitudinal distance increased. The decrease of oxide thickness showed the concentration of the excited oxygen species decreased along the longitudinal direction. It was also found that the oxide thickness increased as the microwave power was increased.

Some properties of the ultrathin oxides grown by microwave plasma afterglow oxidation were studied. The FTIR peak position of Si–O stretching mode in the oxide grown by microwave plasma afterglow oxidation was 1073.8 cm⁻¹. It is near the value in the oxides grown by dry oxidation. The C–V curves and Dₓ plots of capacitors with thickness of 6, 8, and 10 nm as-grown oxide layers were shown. The flatband voltage were between −0.36 and −0.5 V and the effective oxide charge densities were in the range of 1×10¹¹–4×10¹¹ cm⁻². The lowest effective oxide charge density was 8.6×10¹⁰ cm⁻², and the lowest midgap interface state density was about 7.5×10¹⁰ cm⁻² eV⁻¹. The results are superior to the previous ones.

The breakdown fields of the ultrathin oxides was mainly distributed from 7 to 9 MV/cm. The highest breakdown field was 9.5 MV/cm in the 8 nm thick oxide sample. The time-dependent dielectric breakdown characteristics of the ultrathin oxides was also examined. And as the applied electric field was 8 MV/cm, the time to breakdown was 2053 s. The charge to breakdown of the ultrathin oxide was 9.1 C/cm². The relation between the charge to breakdown and injection currents was also demonstrated.
TABLE IV. Properties of the ultrathin oxides grown by microwave plasma afterglow oxidation with ultrasonic vibration modified RCA clean method.

<table>
<thead>
<tr>
<th>Sample description</th>
<th>Thickness ($t_{ox}$) (nm)</th>
<th>Flatband voltage ($V_{fb}$) (V)</th>
<th>Effective oxide charge ($N_{eff}$) (cm$^{-3}$)</th>
<th>Midgap interface state density ($D_{int}$) (cm$^{-1}$ eV$^{-1}$)</th>
<th>Breakdown ($E_{bd}$) (MV/cm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>700 °C, 500 W as-grown</td>
<td>4.1</td>
<td>−0.464</td>
<td>3.1E11</td>
<td>9.6E11</td>
<td>8.20</td>
</tr>
<tr>
<td>700 °C, 500 W as-grown 20 min with ultrasonic vibration modified RCA clean</td>
<td>8.1</td>
<td>−0.376</td>
<td>1.29E11</td>
<td>4.10E11</td>
<td>8.6–8.7</td>
</tr>
</tbody>
</table>

TABLE V. Properties of the ultrathin oxides grown by microwave plasma afterglow oxidation with different treatments.

<table>
<thead>
<tr>
<th>Sample description</th>
<th>Thickness ($t_{ox}$) (nm)</th>
<th>Flatband voltage ($V_{fb}$) (V)</th>
<th>Effective oxide charge ($N_{eff}$) (cm$^{-3}$)</th>
<th>Midgap interface state density ($D_{int}$) (cm$^{-1}$ eV$^{-1}$)</th>
<th>Breakdown ($E_{bd}$) (MV/cm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>700 °C, 500 W as-grown 20 min</td>
<td>8.1</td>
<td>−0.406</td>
<td>1.96E11</td>
<td>2.04E11</td>
<td>8.21</td>
</tr>
<tr>
<td>N$_2$O plasma annealed 15 min</td>
<td>8.3</td>
<td>−0.4712</td>
<td>2.97E11</td>
<td>5.0E11</td>
<td>8.786</td>
</tr>
<tr>
<td>N$_2$O <em>2</em> plasma annealed 15 min</td>
<td>10.8</td>
<td>−0.437</td>
<td>1.7E11</td>
<td>1.68E11</td>
<td>8.60</td>
</tr>
<tr>
<td>HF dipping 10 min</td>
<td>9.0</td>
<td>−0.464</td>
<td>2.73E12</td>
<td>2.74E11</td>
<td>8.53–8.86</td>
</tr>
<tr>
<td>O$_2$ plasma+HCl 20 min</td>
<td>7.6</td>
<td>−0.376</td>
<td>1.38E11</td>
<td>2.37E11</td>
<td>8.64</td>
</tr>
</tbody>
</table>

The modified RCA cleaning with ultrasonic vibration could reduce both the effective charges and interface state densities and also increase the breakdown fields.

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