Electrical properties of thin gate dielectric grown by rapid thermal oxidation

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In this article, we adopted the rapid thermal oxidation (RTO) method to grow gate oxide layers on Si substrates. These RTO oxides were grown in both O2 atmosphere (dry RTO oxide) and in H2 and O2 mixed atmosphere (wet RTO oxide) at above 1000 °C. For comparison, conventional furnace oxides were grown in H2 and O2 mixed atmosphere (furnace wet oxide) as the contrast samples. In this experiment, wet RTO oxides showed better electric characteristics than dry RTO oxides. We also found that a postannealing in nitric oxide (NO) atmosphere can further improve the electric properties of these wet RTO oxides. From these experimental results, we believe that postannealing in NO atmosphere is an effective method to improve oxide electric characteristics. We also found that wet RTO oxide has a superior ability to resist a constant current stress. © 2000 American Vacuum Society. [S0734-2101(00)02706-8]

I. INTRODUCTION

As gate oxide thickness is scaled down in accordance with deep-submicrometer applications, it is also necessary to improve gate oxide reliability in metal–oxide–semiconductor field-effect transistors (MOSFETs). Recently, many methods have been proposed to improve the qualities of thin gate oxides, such as oxide grown in D2O atmosphere, oxynitride gate dielectric grown in nitric oxide (NO) atmosphere, oxide grown in nitrous oxide (N2O) atmosphere, and oxide grown in N2O and O2 mixed atmosphere.1–5 The rapid thermal oxidation (RTO) process has a much shorter thermal budget time than conventional furnace wet oxidation. Thus, in order to prevent impurity redistribution, the RTO process seems to be the best method to grow gate oxides. In this article, we adopted the RTO method to grow thin oxides. The RTO process used in this study was carried out in an in situ steam generation (ISSG) system. The H2, O2, N2, and NO gases were introduced into the ISSG system to act as reactants. During oxidation, the chamber pressure was kept under 100 Torr. As a result, we could precisely control the oxide deposition rate without lowering the oxidation temperature. Prior to oxide growth, in situ high-temperature H2 baking was performed to remove the native oxide on the surface of the silicon wafer.

Previously, it has been reported that nitride oxide can improve electrical properties, such as the breakdown field and reliability of the oxide layers.2–7 In this article, we will discuss the effects of nitrogen injection into oxide during a postannealing process in NO atmosphere. Furthermore, the differences between dry RTO oxides and wet RTO oxides will also be discussed.

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II. EXPERIMENTS

The thin gate oxides used in this study were grown on the p- and n-well silicon substrates at above 1000 °C in an ISSG system. Prior to oxidation, in situ high-temperature H2 baking was used to remove the native oxide on the silicon wafer surface. During the RTO process, hydrogen (H2) and oxygen (O2) gases were introduced to act as reactants. In this article, the oxide grown in O2 atmosphere is called “dry RTO oxide” and that grown in H2 and O2 mixed atmosphere is called “wet RTO oxide.” After oxidation, the oxide layers were all annealed in situ by rapid thermal annealing (RTA) in a N2 or NO ambient at 1050 °C for 60 s. The RTO oxide followed by RTA in N2 gas is called the “RTO N2 oxide.” The RTO oxide followed by RTA in NO gas is called the “RTO NO oxide.” The thickness of the RTO (dry or wet) oxides was about 40 Å. For comparison, conventional furnace oxide grown in H2 and O2 mixed gas at 800 °C followed by furnace thermal annealing in N2 atmosphere at 1000 °C was also prepared. It was called the “furnace wet oxide.” The detailed growth conditions of these thin oxides are listed in Table I. The thicknesses of these films were all measured by an ellipsometer and a Keithly capacitor–voltage (C–V) measurement system at 1 MHz. The oxide thicknesses measured by these methods are listed in Table II.

After oxide growth, the n+ - and p+-polysilicon gate electrodes were deposited, respectively, onto the oxide surface of the p- and n-well region. Subsequently, conventional MOSFET processes were performed to complete the remaining processes. The electric properties of the gate oxide were measured by using an HP 4145 semiconductor parameter analyzer. We used this instrument to measure the electric characteristics of the gate oxide such as current density versus electric field (J–E), breakdown field (Ebd), charge-to-breakdown (Qbd) measurement, carrier mobility (μ), and stress-induced leakage current (SILC).
TABLE I. Specific growth conditions of the furnace wet, dry RTO, and wet RTO oxides with a thickness of 40 Å.

<table>
<thead>
<tr>
<th>Oxide name</th>
<th>Growth conditions</th>
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<tbody>
<tr>
<td>Furnace wet</td>
<td>Furnace (800 °C/40 s)+1000 °C N2 annealing</td>
</tr>
<tr>
<td>Dry RTO N2</td>
<td>RTO O2 (1000 °C/15 s, 100 Torr)+N2 RTA</td>
</tr>
<tr>
<td>Dry RTO NO</td>
<td>RTO O2 (1000 °C/13 s, 100 Torr)+NO RTA</td>
</tr>
<tr>
<td>Wet RTO N2</td>
<td>RTO H2+O2 (1050 °C/21 s, 10 Torr)+N2 RTA</td>
</tr>
<tr>
<td>Wet RTO NO</td>
<td>RTO H2+O2 (1000 °C/20 s, 10 Torr)+NO RTA</td>
</tr>
</tbody>
</table>

III. RESULTS AND DISCUSSION

The capacitors, which we used to measure the current density (J) versus electric-field (E) characteristic, were square with an area of 4 × 10^{-6} cm². The negative and positive voltage were, respectively, biased to the n⁺- and p⁺-polysilicon gate electrodes. Figure 1 shows the typical curves of the current density versus electric field (J vs E) for the metal–oxide–semiconductor (MOS) capacitors with furnace wet, dry RTO, and wet RTO oxides. We can clearly find that the wet RTO oxides exhibit a higher breakdown field and a lower leakage current than the dry RTO oxides for both p- and n-well capacitors. This can be attributed to the number of defects existing in these oxides. It has been pointed out that wet oxidation can be used to effectively shrink or reduce the number of as-grown defects in the oxide. It is also well known that the defects can enhance the carriers to tunnel through the gate oxide. Thus, dry RTO oxides exhibit a lower leakage current and a higher breakdown field due to the larger number of defects. It can also be found from Fig. 1 that wet RTO oxide followed by NO postannealing treatment showed a higher breakdown field. This result can be attributed to the incorporation of oxygen and nitrogen atoms in the gate oxide. Previously, Hori, Iwasaki, and Tsuji have reported that hydrogen-related electron trapping could lower the gate oxide quality. Hydrogen-related bonds can be broken during high-temperature postannealing. When the hydrogen atoms leave the oxide layer, new dangling bonds are formed. As a result, more traps will exist in the oxide. On the other hand, nitride oxide can be easily decomposed into excited oxygen and nitrogen atoms during postannealing. These excited atoms can effectively incorporate with the dangling bonds to form Si–O or Si–O–N bonds in the oxide. Therefore, it can effectively reduce the electron traps in the as-grown oxide and suppress the leakage current. Furthermore, the nitrogen pileup at the SiO2/Si interface can effectively reduce the interface strain, so the nitrided oxide can also enhance the SiO2/Si interface strength. As a result, the breakdown field can also be effectively enhanced. For the wet RTO oxide postannealed in N2 atmosphere, the electric characteristic did not show any significant improvement since nitrogen gas (N2) cannot be easily decomposed into excited nitrogen atoms (N).

Dry oxide has a much smaller amount of hydrogen-related traps in the oxide. Thus, dry RTO oxide followed by NO postannealing will not show any obvious improvement in electric characteristics than that followed by the N2 postannealing, although the nitride oxide is also formed in the dry RTO oxide. They almost possess the same current–voltage characteristic. Previously, it has been shown that wet oxidized SiO2 film has a smoother interface than dry oxidized SiO2 film. It has also been pointed out that the growth rate of dry RTO oxide is faster than that of the wet RTO oxide, although dry RTO oxide had also been annealed in NO ambient. But, its rough interface might still be the dominant factor affecting the current–voltage characteristic of the oxide. As a result, NO postannealing will not significantly reduce the leakage current of the dry RTO oxide, as can be seen from Fig. 1.

Before dielectric breakdown, the leakage current of the furnace wet oxide was almost equal to that of the wet RTO N2 oxide. Although the furnace wet oxide grown at a low temperature (800 °C) will induce a larger stress at the SiO2/Si interface, a postannealing at the same high temperature (1000 °C) can effectively reduce the interface strain. Furthermore, the long oxidation and postannealing time can provide enough duration to complete the chemical reaction and relax the stress in the oxide. Therefore, furnace wet oxide grown at a low temperature followed by high-temperature annealing will exhibit a leakage current characteristic that is similar to that of the wet RTO N2 oxide grown at a high temperature.

Figures 2(a) and 2(b) show the Weibull plot of the breakdown field (Ebd) measurement for furnace wet, dry RTO, and wet RTO oxides for p- and n-wells, respectively. The breakdown field is defined as the oxide breakdown voltage divided by the oxide thickness measured by Keithly high-frequency C–V measurement. The n⁺- and p⁺-polysilicon gate electrodes were, respectively, negative and positive biased to the p- and n-well regions. The capacitor’s area is 10^{-2} cm². From Figs. 2(a) and 2(b) we can clearly see that wet RTO oxides exhibit higher breakdown fields than dry RTO oxide. Also, the breakdown field of the wet RTO oxide is higher than that of the furnace wet oxide. These results agree well with those shown in Fig. 1. As can be seen from Figs. 2(a) and 2(b), the wet RTO NO oxide always shows the highest breakdown field for both p- and n-well MOS capacitors.

The charge-to-breakdown (QBD) measurement is another method to verify the oxide quality. The charge-to-breakdown, (QBD), defined as the total quantity of the

TABLE II. Oxide thickness measured by the ellipsometry and Keithly high-frequency C–V measurement for furnace wet, dry RTO, and wet RTO oxides.

<table>
<thead>
<tr>
<th>Oxide name</th>
<th>Ellipsometry</th>
<th>Keithly C–V</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Tox (Å)</td>
<td>Tn (Å)</td>
</tr>
<tr>
<td>Furnace wet</td>
<td>41.8</td>
<td>39.6</td>
</tr>
<tr>
<td>Dry RTO N2</td>
<td>41.9</td>
<td>40.8</td>
</tr>
<tr>
<td>Dry RTO NO</td>
<td>41.3</td>
<td>42.0</td>
</tr>
<tr>
<td>Wet RTO N2</td>
<td>41.6</td>
<td>40.7</td>
</tr>
<tr>
<td>Wet RTO NO</td>
<td>41.6</td>
<td>39.5</td>
</tr>
</tbody>
</table>
charge passing through the oxide before the oxide breakdown, is used to analyze the reliability of the oxide film. In our experiment, the same constant current density of 100 mA/cm² was stressed onto every MOS capacitor. The capacitor’s area is $10^{-2}$ cm². Figures 3a and 3b show the Weibull plot of the charge to breakdown for the p- and n-well MOS capacitors under constant current stress, respectively. For the p-well MOS capacitor, a negative bias was applied to its n-polysilicon gate electrode. For the n-well MOS capacitor, a positive bias was applied to its p-polysilicon gate electrode.

The breakdown mechanism of the dielectric is related to the charge trapping in the dielectric. The hydrogen atoms in the bulk SiO₂ and at the SiO₂/Si interface will react with the silicon dangling bonds to form Si–H or Si–OH bonds.12 Hot electrons will then break these hydrogen-related bonds during the constant current stress. After the hydrogen atoms are released from the Si–H or Si–OH bonds, the remaining vacancies will thus become electron-trapping sites to degrade the reliability of the gate oxide. Since the growth temperature of the RTO oxide is higher than that of the furnace wet oxide, RTO could thus effectively reduce the formation of hydrogen-related bonds in the bulk SiO₂ and at the SiO₂/Si interface. Although the number of hydrogen-related bonds in dry oxide is smaller than the number of hydrogen-related bonds in wet oxide, dry RTO oxide still exhibits the worst reliability than the others due to the large number of as-grown defects.

Figure 4 is the stress-induced leakage current measurement. The curves are the leakage current variation versus the stress time for furnace wet, dry RTO, and wet RTO oxides. The vertical axis is the leakage current variation of the oxide.

**Fig. 1.** Curves of current density vs electric field for MOS capacitors with furnace wet, dry RTO, and wet RTO oxides (a) p well and (b) n well ($T_{\text{ox}} = 40 \text{ Å}$, capacitor area=$4 \times 10^{-6} \text{ cm}^2$).

**Fig. 2.** Weibull plot of the breakdown field for MOS capacitors with furnace wet, dry RTO, and wet RTO oxides (a) p well and (b) n well ($T_{\text{ox}} = 40 \text{ Å}$, capacitor area=$10^{-2} \text{ cm}^2$).
before and after constant current stress. The stress time is continuous from 10 to 4000 s under constant current. For preventing the occurrence of oxide breakdown in a short time, the stress current density is maintained at 10 mA/cm². The stress current is different from the applied current density of 100 mA/cm² of the \( Q_{BD} \) measurement in Fig. 3. The capacitor’s area is \( 10^{-2} \) cm². From the \( Q_{BD} \) measurement, we know the dry RTO oxide easily encounters dielectric breakdown. For avoiding dry RTO oxide breakdown, the stress time is continuous from 10 to 1300 s for dry RTO oxides. The leakage current density is decided while the electric field \( E_g \) applied to the oxide is 9 MV/cm. By comparing the \( p \)- and \( n \)-well capacitors, we found the \( n \)-well capacitors had a better ability to suppress stress-induced leakage current and to prevent dielectric breakdown than the \( p \)-well capacitors. This phenomenon can be attributed to the difference of the interface barrier potential. The electron injection direction is opposite for \( p \)- and \( n \)-well capacitors. Therefore, \( p \)- and \( n \)-well capacitors will exhibit different characteristics. For \( p \)-well capacitors, the furnace wet oxide shows the smallest variation of stress-induced leakage current below the stress time of 2000 s. When the stress time is over 2000 s, the capacitors of the furnace wet oxide and wet RTO N₂ oxide were broken down. Then, only the wet RTO NO oxide could be continuously operated. For \( p \)-well capacitors, the wet RTO NO oxide shows the smallest variation of stress-induced leakage current. At the stress time of 3000 s, variation of the stress-induced leakage current of the furnace wet oxide abruptly increased and became larger than the wet RTO N₂ oxide. When the stress time is over 3000 s, the capacitor of the furnace wet oxide was broken down. Then, the amount of charges passing through the furnace wet oxide is almost less than 30 C/cm² before the occurrence of the oxide breakdown. This result agrees with the \( Q_{BD} \) measurement of the furnace wet oxide in Fig. 3, although the stress current density in the SILC measurement is smaller than that (100 mA/cm²) in the \( Q_{BD} \) measurement. The wet RTO oxide still exhibits a superior ability to resist the constant current stress.

The stress existing at the SiO₂/Si interface is caused by the volume expansion of the SiO₂ films. After the constant current stress, the chemical bonds of the oxide with a larger strain will be broken easily. Weak bonds such as Si–H and Si–OH will also be broken. These broken chemical bonds will result in a large number of defects. Thus, the leakage current will also become larger. The incorporation of nitrogen atoms into the oxide is an effective method to relax the stress at the SiO₂/Si interface. Since NO can be decomposed into excited oxygen and nitrogen atoms easily, nitro-
gen atoms can be injected into the oxide to reduce the stress when the oxide is annealed at NO environment. Thus, wet RTO oxides followed with a NO postannealing will exhibit a lower leakage current than that followed with a N2 postannealing after constant current stress. Also, since dry oxide has more defects than wet oxide, the dry RTO oxide will exhibit a higher leakage current than the wet RTO oxide after constant current stress. Such a large leakage current can break the weak bonds easily and cause the oxide to breakdown.

Figures 5(a) and 5(b) show the normalized effective carrier mobility as a function of the effective electric field for $n'$ and $p'$ MOSFET (W/L = 10 μm/10 μm) with furnace wet oxide, dry RTO oxide, and wet RTO oxide. The voltages applied to the drain of the $n'$ and $p'$ MOSFET are 0.05 and −0.05 V, respectively. By normalizing the carrier mobility, we can clearly observe the degradation rate of the carrier mobility, which depends strongly on the SiO2/Si interface. From Figs. 5(a) and 5(b) we can clearly find that the degradation of the electron mobility of the furnace wet oxide is slower than the RTO oxides for $n'$ MOSFET. Similar phenomena are also observed for $p'$ MOSFET. We believe that these observations are due to the fact that the process time of the RTO oxide is shorter than that of the furnace wet oxide. Thus, the interface roughness of the RTO oxide is more serious than the furnace wet oxide. From Fig. 5, we believe that interface roughness is the main factor affecting the carrier mobility of the furnace wet and RTO oxides. On the other hand, the fast degradation of carrier mobility of the RTO oxide can be improved by properly increasing the process time.

At low electric field, the carriers travel away from the SiO2/Si interface. As a result, carrier mobility will not be strongly influence by the interface quality. When higher voltage is applied to the gate electrode, more carriers were induced and the induced carriers are closer to the SiO2/Si interface. Thus, the importance of the interface scattering effect will increase. The carrier-carrier scattering probabilities will also increase. As a result, the carrier mobility will degrade significantly under high voltage.

Since the defects existing in the oxide can trap the induced carriers, it will also affect the carrier mobility. We know that wet oxide has fewer defects and a smoother interface than dry oxide. Thus, the degradation rate of the carrier mobility of the wet RTO oxide was slower than the dry RTO oxide, as can be seen from Figs. 5(a) and 5(b). Furthermore, we know that postannealing in NO atmosphere can effectively reduce the acceptor-like interface state in the oxide.

Thus, the oxides with NO postannealing show a slower degradation of carrier mobility than that with a N2 postannealing, as can be seen from Figs. 5(a) and 5(b).

IV. CONCLUSION

The electrical properties of thin oxides grown by rapid thermal oxidation in an in situ steam generation system at low pressure and high temperature were examined. From the experimental results, we found that dry oxide had worse electric characteristics than wet oxide. In this experiment, the furnace wet oxide acted as the contrasting object. Compared with the furnace wet oxide, the wet RTO oxide shows a superior ability to resist constant current stress. For the measurements of the breakdown field and charge to breakdown, the wet RTO oxide also exhibits better electric characteristics. Furthermore, the wet RTO oxide followed with a NO postannealing can effectively enhance the oxide breakdown field, oxide reliability, and slower degradation of carrier mobility. Although the carrier mobility of the RTO wet NO oxide was worse than the furnace wet oxide, the RTO process effectively improves the thermal budget. Whatever the postannealing, nitric oxide atmosphere is still a recommended method for improving oxide electric properties.

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