Highly Reliable Thin Nitrided SiO₂ Films Formed by Rapid Thermal Processing in an N₂O Ambient

Hisashi FUKUDA, Tomiyuki ARAKAWA and Seigo OHNO
Semiconductor Tech. Lab., Oki Electric Industry Co., Ltd.
550-5 Higashiasakawa, Hachioji, Tokyo 193, Japan

Nitridation of thin SiO₂ film has been succeeded by rapid thermal processing (RTP) using only O₂ and N₂O as reactants. In comparison with pure SiO₂ film, nitrided SiO₂ (SiOₓNᵧ) film (8 nm), which includes about 5 at% nitrogen, at the SiOₓNᵧ/Si interface, showed a large charge-to-breakdown value greater than 30 C/cm² and a density of electron traps lower than that of SiO₂ in high-field stressing (>8 MV/cm) under the condition of gate negatively biased. The SiOₓNᵧ/Si interface evaluated by high-resolution TEM is quite uniform, at least ordered within one or two atomic layers.

1. INTRODUCTION

Very thin SiO₂ films are strongly needed for advanced integrated circuits such as scaled EPROMs, EEPROMs and MOSFETs. In these MOS devices, dielectric films should have excellent leakage characteristics and high dielectric strength. The trapping characteristics are also important for keeping device reliability. The wear-out and hot-carrier injection of SiO₂ film due to high-field stress become to be more actualized with a decrease in the SiO₂ film thickness. To improve the dielectric properties, thermal nitridation of SiO₂ has been proposed.¹⁻³ Many activities in this field have been focused on the nitridation of SiO₂ with NH₃. Although NH₃-nitried SiO₂ film has several advantages such as reduction of the interface trap states and blocking of impurity penetration, the inclusion of hydrogen atoms (H), which act as an origin of electron traps, is unavoidable. Reoxidation of this film has been proved to be effective in reducing included H atoms.⁴⁻⁶ To avoid the above complexity, we have successfully applied rapid thermal processing (RTP) to the nitridation of thin SiO₂ films. This process consists of the combination of in situ oxidation with O₂ and in situ nitridation with nitrous oxide (N₂O). In this paper, the dielectric properties of N₂O-nitrided SiO₂ (SiOₓNᵧ) film and the SiOₓNᵧ/Si interface structure will be described in comparison with pure SiO₂ film.

2. EXPERIMENTAL

SiO₂ and SiOₓNᵧ films were formed on 3-5 ohm cm, p-type (100) Si wafers after the standard cleaning procedure reported elsewhere.⁷,⁸) by the above oxidation and nitridation (or oxynitridation), in which the heating and cooling rates were 50-100°C/s. Table I shows the process sequences employed. For all samples #1, #2, #3 and #4, the total film thicknesses were 8.2 nm ± 0.5 nm. MOS capacitors were fabricated by depositing n⁺ polysilicon gate electrodes on the dielectric films. MOS characteristics were evaluated by C-V, I-V and time-dependent dielectric breakdown (TDDB) measurements. The SiOₓNᵧ/Si
interface was evaluated by high resolution TEM (HRTEM), Auger electron spectroscopy (AES) and X-ray photoelectron spectroscopy (XPS).

### 3. RESULTS

#### 3.1 Dielectric properties of SiO\textsubscript{x}N\textsubscript{y} films

To investigate the effect of stress on the MOS capacitors, electrons were injected, in the Fowler-Nordheim (F-N) region, from the gate electrode into the dielectric films at a constant current (-10 mA/cm\textsuperscript{2}). All measurements were performed on MOS capacitors with the gate area of 2x10\textsuperscript{-4} cm\textsuperscript{2}.

The effect of the stress on the density of Interface trap states (D\textsubscript{It}) as a function of injected charge (Q\textsubscript{inj}) is shown in Fig.1. Sample #1 (pure SiO\textsubscript{2}) showed a large increase in D\textsubscript{It} at the initial stage. On the contrary, samples #2, #3 and #4 (SiO\textsubscript{x}N\textsubscript{y}) provide smaller ΔD\textsubscript{lt} values as compared to sample #1. Figure 2 shows the effect of the stress on the flatband voltage shifts (ΔV\textsubscript{FB}). Although negative shifts of V\textsubscript{FB} are found for all samples, the shifts of samples #2, #3 and #4 are much smaller than that of sample #1. The amount of ΔV\textsubscript{FB} corresponds to the density of hole traps. Hence, the saturation tendency of V\textsubscript{FB} in higher charge region exhibits hole trap filling process.

The gate voltage shifts (ΔV\textsubscript{g}) at a constant current density are plotted in Fig.3. For sample #1, V\textsubscript{g} is slightly shifted to the positive direction at the initial stage, and then increases almost linearly to the negative direction with increasing Q\textsubscript{inj}. This nonsaturating increase of V\textsubscript{g} is

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<th>No.</th>
<th>RTON-1</th>
<th>RTO</th>
<th>RTON-2</th>
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<tbody>
<tr>
<td>#1</td>
<td>------</td>
<td>0\textsubscript{2}.1100°C</td>
<td>------</td>
</tr>
<tr>
<td>#2</td>
<td>N\textsubscript{2}0.1100°C</td>
<td>0\textsubscript{2}.1100°C</td>
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<tr>
<td>#3</td>
<td>N\textsubscript{2}0.1100°C</td>
<td>0\textsubscript{2}.1100°C</td>
<td>N\textsubscript{2}0.1100°C</td>
</tr>
<tr>
<td>#4</td>
<td>------</td>
<td>0\textsubscript{2}.1100°C</td>
<td>N\textsubscript{2}0.1100°C</td>
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![Fig.1 Interface trap density change as a function of the injected charge for samples #1-#4.](image1)

![Fig.2 Flatband voltage shift as a function of the injected charge for samples #1-#4.](image2)

![Fig.3 Gate voltage shift as a function of the injected charge for samples #1-#4.](image3)
attributed to the creation of new electron traps. On the contrary, for samples #2, #3 and #4, no positive Vg shifts are observed and the degrees of negative Vg shifts are much smaller than that in sample #1. As is seen in Fig.3, charge-to-breakdown (QBD) increased in the order: sample #2, #3, #1 and #4.

Figure 4 shows cumulative TDDB failures for all samples. It is apparent that sample #4 is superior to sample #1, but samples #2 and #3 are much inferior to sample #1. This finding indicates that proper nitridation (sample #4) is effective for improving the breakdown characteristics.

3.2 The SiOxNy/Si interface structure
The layer compositions of the oxide films were investigated by AES. The depth profiles of N, O and Si for sample #1 are shown in Fig.5. Nitrogen is not observed in the bulk or at the SiO2/Si interface within detection limits. On the contrary, an accumulation of N of about 5 at% was observed at the interface of sample #4, as shown in Fig.6. Similar results were obtained for samples #2 and #3.

The chemical bonding state of N atoms at the SiOxNy/Si interface was investigated by XPS. Typical O(1s) and N(1s) core level spectra measured near the interface of sample #4 is shown in Fig.7. The N(1s) peak due to Si-N bonds is found at 397.8 eV. The O(1s) spectrum, whose main peak appears at 532.2 eV, indicates that the SiOxNy structure is essentially the same as tetrahedral SiO4 itself.

The morphology of the SiOxNy/Si interface was evaluated by HRTEM. As shown in Figs.15 and 16, the SiOxNy/Si interface is defined by the presence of Si-O-Si bonds, which are stable and resistant to oxidation.

Fig.4 Cumulative failure-stress time relationships in the TDDB test of samples #1-#4.
Fig.5 Auger depth profile of sample #1.
Fig.6 Auger depth profile of sample #4.
Fig.7 O(1s) and N(1s) core level lines in XPS spectra for sample #4.
in Fig. 8, HRTEM images show that the SiO\textsubscript{x}N\textsubscript{y}/Si interface in sample #4 is quite uniform at least ordered within one or two atomic layers, whereas undulation up to 1 nm and thickness inhomogeneity are observed in samples #2 and #3.

4. DISCUSSION

The SiO\textsubscript{x}N\textsubscript{y} film formed by RTP indicates smaller changes in the densities of electron and hole traps and in Dit as compared with SiO\textsubscript{2} film.

These differences between the pure SiO\textsubscript{2} and SiO\textsubscript{x}N\textsubscript{y} film can be explained on the basis of the broken bond model\textsuperscript{9-11}. In SiO\textsubscript{2} film, defects such as strained Si-O, Si-0-0-Si and/or Si-OH groups are present. This model indicates that when the above defects are scissored off by injected electrons, a large number of trivalent silicon, Si\textsuperscript{+} (O\textsubscript{3}\equiv Si\textsuperscript{+} and/or Si\textsubscript{3}≡Si\textsuperscript{+}), which act as hole traps, is generated and that they induce positive charge by processes such as O\textsubscript{3}≡Si\textsuperscript{+} + h\textsuperscript{+} → O\textsubscript{3}≡Si\textsuperscript{+}. Injected electrons are captured simultaneously by the process: O\textsubscript{3}≡Si\textsuperscript{+} + e\textsuperscript{-} → O\textsubscript{3}≡Si\textsuperscript{+}. If the above Si\textsuperscript{+} defects are minimized by the formation of Si-N bonds near the SiO\textsubscript{x}N\textsubscript{y}/Si interface, the hole trapping rate can be reduced, resulting in decreases ΔD\textsubscript{it} and in positive charge density. The formation of Si-N bonds plays also an important role in reducing electron traps.

In the V\textsubscript{g} measurements, only sample #4 showed a large Q\textsubscript{BD} value greater than 30 C/cm\textsuperscript{2} as compared to that of sample #1. On the contrary, Q\textsubscript{BD} values for samples #2 and #3 are much smaller than that of sample #1. The detailed mechanism of breakdown phenomena is still unknown. However, for samples #2 and #3, film thickness inhomogeneity and large undulation at the interface have been confirmed by HRTEM. Hence, we consider that localization of electric field and charge build up occur in samples #2 and #3, resulting in smaller Q\textsubscript{BD} values. On the other hand, sample #4 has atomically flat interface as is similar to thin SiO\textsubscript{2} film previously reported\textsuperscript{7,8}, consistent with its excellent dielectric properties.

5. CONCLUSION

A new and reliable method of nitridation of thin SiO\textsubscript{2} film has been developed by employing the following RTP sequence: oxidation in O\textsubscript{2} and nitridation (or oxynitridation) in N\textsubscript{2}O. The dielectric properties of SiO\textsubscript{2} film can be greatly improved by this process.

REFERENCES