Role of SiN Bond Formed by N$_2$O-Oxynitridation for Improving Dielectric Properties of Ultrathin SiO$_2$ Films

Makoto YASUDA, Hisashi FUKUDA, Toshiyuki IWABUCHI and Seigo OHNO
Semiconductor Tech. Lab., Oki Electric Industry Co., Ltd. 550-5 Higashisakawa, Hachioji, Tokyo 193, Japan

Dielectric properties of rapid-thermally N$_2$O-oxynitrided (RTON) ultrathin (5-10nm) SiO$_2$ films have been investigated. High-field endurance characteristics indicate that the RTON SiO$_2$ film has a much smaller electron trap generation rate, a lower field-induced leakage current and a larger charge-to-breakdown, as compared to those of RTO SiO$_2$ and NH$_3$-nitrided (RTN) SiO$_2$ films. Moreover, it has been clarified from FT-IR, AES and XPS measurements that strong Si-N bonds are formed at the SiO$_2$/Si interface by RTON, whereas a large amount of N-H and Si-H bonds, which act as electron traps, are generated by RTN.

1. INTRODUCTION

To realize the integrity and good reliability of ultrathin (5-10nm) SiO$_2$ film will be strongly required owing to continuing demands of scaling down of VLSI/ULSIs. This issue becomes more crucial for scaled floating gate memories, such as advanced EPROMs, EEPROMs and flash memories, in which the data retention time as well as write/erase cycles is limited by the oxide wear out [1,2]. In the last decade, thermal nitridation of SiO$_2$ film in NH$_3$ has been studied as an alternative for conventional gate and tunneling insulators because of the reliability problem of thin SiO$_2$ film [3,4]. In fact, NH$_3$-nitrided SiO$_2$ films are more radiation resistant, less permeable to diffusing impurities and less susceptible to process related damage. However, breakdown degradation has been also observed by certain researchers [5]. To obtain long-term reliability of NH$_3$-nitrided SiO$_2$ film, reoxidation of nitrided SiO$_2$ film has also attracted much attention [6-8]. Reoxidation of nitrided SiO$_2$ film produces the reduction of interface trap state generation and excellent breakdown characteristics. This process is, however, rather complicated and strongly dependent on its process conditions.

We have recently achieved for the first time a new method for forming highly reliable oxynitrided SiO$_2$ film by using O$_2$ and N$_2$O as reactants [9-11], and successfully applied it to the gate oxide of sub-halfmicron CMOSFETs [12]. In this paper, the dielectric properties of N$_2$O-oxynitrided ultrathin SiO$_2$ films will be demonstrated. Then, the role of SiN bond formed by this N$_2$O-oxynitridation on the dielectric properties of ultrathin SiO$_2$ film will be discussed.

2. EXPERIMENTAL

The dielectric films were formed on 5-8 ohm-cm, n-type (100)-oriented Si wafers (5 inch) after a standard cleaning procedure reported elsewhere [13]. Rapid thermal processing (RTP) apparatus used was equipped with tungsten-halogen lamp heaters and with an oil-free high-vacuum pumping system. Table 1 shows the process sequences employed. In each process, ambient gases were rapidly switched off between rapid thermal oxidation (RTO) and rapid thermal oxynitridation (RTON). MOS capacitors were fabricated by depositing n+-polysilicon and delineating it to have an area of 2x10$^{-4}$cm$^2$ on the dielectric films. MOS characteristics were studied by I-V and time-dependent dielectric breakdown (TDDB) test for both polarity bias stresses. Film composition and its chemical bonds were evaluated by Auger electron spectroscopy (AES), X-ray photoelectron spectroscopy (XPS) and FT-IR attenuated total reflection (FT-IR ATR) measurements.

3. RESULTS & DISCUSSION

3.1 Dielectric properties of oxide films

The charge trapping and breakdown characteristics were investigated. The gate voltage shifts (ΔV$_g$) under constant current
Anomalous low serious bulk understood produces value RTON Qsn(+). Qsn(+) increased trap type the low-field characteristics data low-field generation of electron traps induced by constant current stress. Thus, the trap generation rate increases in the order; #3, #1 and #2.

Fig. 2 shows the oxide film thickness dependence of charge-to-breakdown (QBD) for samples #1–#4. For positive bias stress, QBD(+) increased with decreasing oxide film thickness. In the oxide thickness region of 5–6nm, RTON SiO₂ films (#3 & #4) have larger QBD(+) values as compared to those of samples #1 and #2. For negative bias stress, the tendency is somewhat different from that of positive bias stress, that is, QBD(-) generally decreases as thinning oxide film thickness. However, only the QBD(-) value for RTON SiO₂ (#3) seems to be slightly higher than those of samples #1, #2 and #4. As for a lower QBD(-) value in RTON SiO₂ (#4), the reason is still unclear. One explanation is that the local field enhancement due to the SiO₂/Si interface roughness and/or oxide thickness inhomogeneity causes lower QBD(-) value [10]. As thinning oxide film thickness, low-field leakage through SiO₂ is gradually increased by Fowler-Nordheim electron injection [12]. This oxide leakage is the most serious limiting factor, that is, produces lower W/E cycles resulting in data retention degradation [1,2]. Typical I-V characteristics of 6nm-thick oxide films before and after stresses are shown in Fig.3. Anomalous leakage occurs in the low-field side (<10MV/cm) at both stresses. This behavior is remarkable for RTON SiO₂ (#2), but not for RTON SiO₂ (#3 & #4). The nature of the low-field conduction is not well understood at this time, however, it does seem to be well fitted by Fowler-Nordheim type conduction mechanism [13]. Moreover, this new finding is closely related to the small $V_g$ shift of N₂O-oxyxnitridation, that is, connected with the small rate of electron trap generation, as shown in Fig.1. This result can be also explained in terms of the idea that N atoms piled up at the SiO₂/Si interface make the trap sites reduced [8].

### 3.2 Physical properties of oxide films

The depth profiles of N atoms evaluated by AES measurements are shown in Fig.4. For RTO SiO₂(#1), N atoms are not observed in the bulk and/or at the SiO₂/Si interface within detection limits. On the contrary, for samples #2–#4, an accumulation of N atoms was

<table>
<thead>
<tr>
<th>No.</th>
<th>$\theta_{ox}$</th>
<th>RTO</th>
<th>RTON (RTN)</th>
</tr>
</thead>
<tbody>
<tr>
<td>#1</td>
<td>6–10nm</td>
<td>O₂,1100℃,4–20ns</td>
<td></td>
</tr>
<tr>
<td>#2</td>
<td>6–10</td>
<td>O₂,1100℃,4–20ns → NH₃,1000℃,30ns</td>
<td></td>
</tr>
<tr>
<td>#3</td>
<td>6–10</td>
<td>O₂,1100℃,2–12ns → N₂O,1100℃,4–34ns</td>
<td></td>
</tr>
<tr>
<td>#4</td>
<td>5–6</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Table 1. Preparation sequences of N₂O-oxyxnitridated, pure SiO₂ and NH₃-nitrided SiO₂ films.

![Fig.1 Gate voltage shift ($\Delta V_g$) as a function of stress time $\theta_{ox}$. $\theta_{ox} = \pm 100mA/cm^2$.](image)

![Fig.2 Oxide film thickness dependence of charge-to-breakdown (QBD) under the same stress condition. $\theta_{ox} = \pm 100mA/cm^2$.](image)
observed at the SiO\textsubscript{2}/Si interface.

The densities of NH, SiH, SiOH and H\textsubscript{2}O bonds in the oxide films were measured by FT-IR ATR. In the FT-IR ATR measurement, SiN vibrations occur in a frequency region masked by SiO\textsubscript{2} mode, and are not accessible experimentally. Thus, the SiN bond density was evaluated by XPS analysis. The results of FT-IR ATR and XPS measurements are summarized in Table 2. In RTN SiO\textsubscript{2} films (#3 & #4), as anticipated, no H-related species such as NH, SiH bonds, which act as electron traps, are present. On the contrary, by RTN process, these species generate. It is considered that electron trapping in high-field stress is associated with chemical reactions such as O\textsubscript{2} + Si-H + e\textsuperscript{-} \rightarrow O\textsubscript{2} + Si\textsuperscript{+} + H\textsuperscript{0}. If these weak H-related species are replaced by Si-N bonds, the electron trapping densities can be reduced. The electron traps may also induce the conduction via trapping sites and closely related to the high-field induced anomalous leakage. In fact, it is noted here that when strong Si-N bonds (4.6eV) are formed without N-H bonds, the capture cross-section of electrons can be reduced. As a result, much slower electron trap generation makes reduce high-field induced leakage current, resulting in a large \( \Phi_{BB} \) value.

**4. CONCLUSION**

We have studied N\textsubscript{2}O-oxynitridation for improving dielectric properties of SiO\textsubscript{2} films. By this technology, ultrathin (5-10nm) SiO\textsubscript{2} films are obtained with a small rate of electron trap generation, a large charge-to-breakdown and high-field induced leakage current. These excellent characteristics of N\textsubscript{2}O-oxynitrided SiO\textsubscript{2} film are originated from strong Si-N bond formation in the SiO\textsubscript{2} film.

**REFERENCES**