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Highly Reliable N_2O-Oxynitrided Tunnel Oxides for Flash Memory

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Cycling of up to 10^6 is confirmed in a flash memory cell with N_2O-oxynitrided SiO_2 as a tunnel oxide. This improvement is shown to be realized by annealing a SiO_2 film in N_2O ambient in a conventional furnace. XANES (X-ray Absorption Near Edge Structure) analysis clarifies that the higher resistance of an oxynitrided SiO_2 film to high electric-field stress is due to the presence of fewer unstable Si - O bonds than in conventional SiO_2 film.

Introduction

Strong program/erase (P/E) endurance is very important in higher-density flash memories, especially for upcoming silicon file applications. Therefore, the resistance of a tunnel oxide to high electric-field stress applied during P/E operations is a key factor in obtaining more reliable memory cells. Recently, light nitridation of SiO_2 with NH_3 or N_2O has been shown to improve the reliability of tunnel oxides (1, 2). In this paper, we demonstrate the effects of N_2O oxynitridation on the resistance of MOS capacitors to high electric-field stress and the program/erase endurance of flash memory cells(3). The mechanism of the improved resistance to high electric-field stress is discussed based on XANES analysis.

Experiments

Pyrogenic SiO_2 was grown with hydrogen and oxygen at 850°C. The N_2O-oxynitrided SiO_2 was grown in a conventional furnace in N_2O at 1000 - 1050°C after SiO_2 formation. Then, post-oxidation annealing was performed in pure N_2 at the same temperature as oxynitridation. The total tunnel oxide thickness was 6.5 - 9 nm. The nitrogen profile in N_2O-oxynitrided SiO_2 is measured by SIMS (Fig. 1). The gate electrode was insitu phosphorous doped poly-Si at a density of 3×10^{20} cm^{-3} formed by LPCVD using Si_2H_6 and PH_3.

The memory cell is programmed through the drain by tunneling electron ejection and erased through the whole channel area by tunneling electron injection (3).

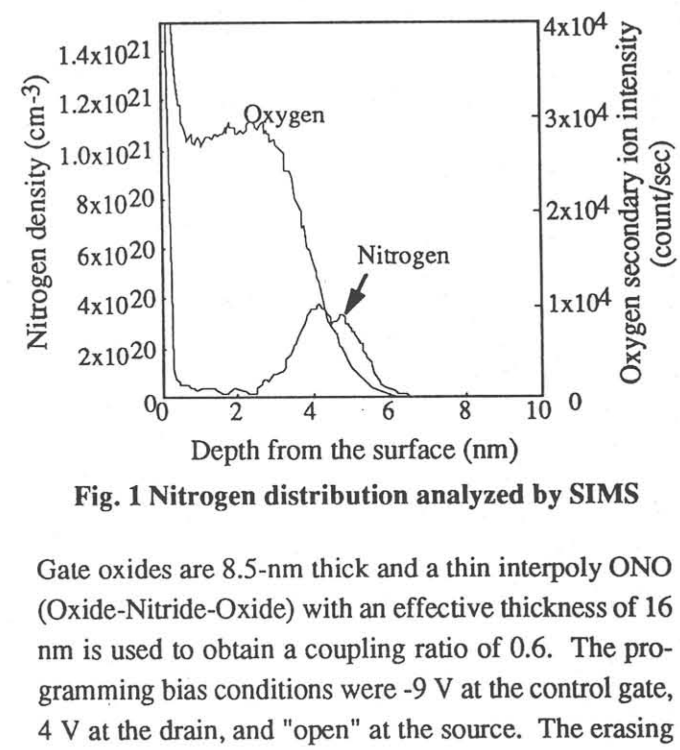

Fig. 1 Nitrogen distribution analyzed by SIMS

Gate oxides are 8.5-nm thick and a thin interpoly ONO (Oxide-Nitride-Oxide) with an effective thickness of 16 nm is used to obtain a coupling ratio of 0.6. The programming bias conditions were -9 V at the control gate, 4 V at the drain, and "open" at the source. The erasing bias conditions were 16 V at the control gate and 0 V at the drain and source.

XANES analysis by synchrotron radiation was conducted to investigate the dielectric structures.

Results and Discussion

We investigated the high electric-field resistance of poly-Si-gate MOS capacitors using N_2O-oxynitrided SiO_2 as a tunnel oxide. Leakage current variance was measured at a constant voltage of 10 V (Fig. 2). The current of both pyrogenic and N_2O-oxynitrided SiO_2 capacitors increases at the beginning of injection, and decreases after saturation. The maximum current ratio

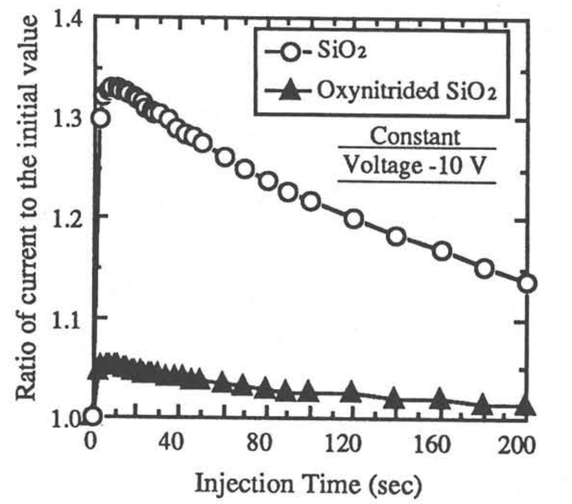

Fig. 2 Leakage-current variance suppression by oxynitridation

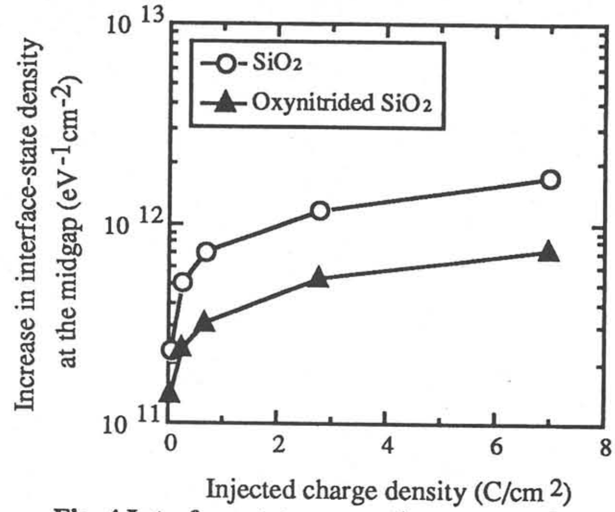

Fig. 4 Interface-state generation suppression by oxynitridation

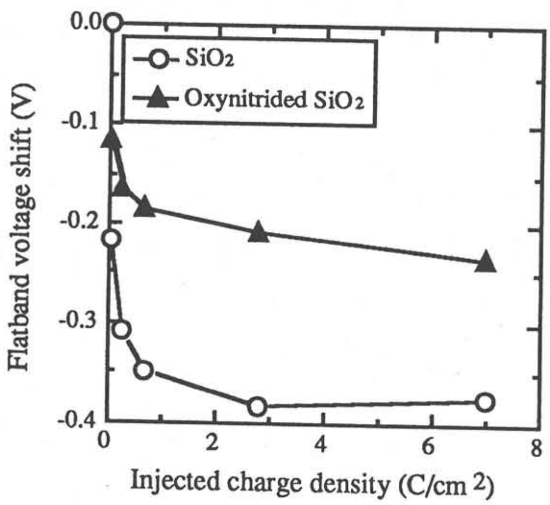

Fig. 3 Flatband voltage shift suppression by oxynitridation

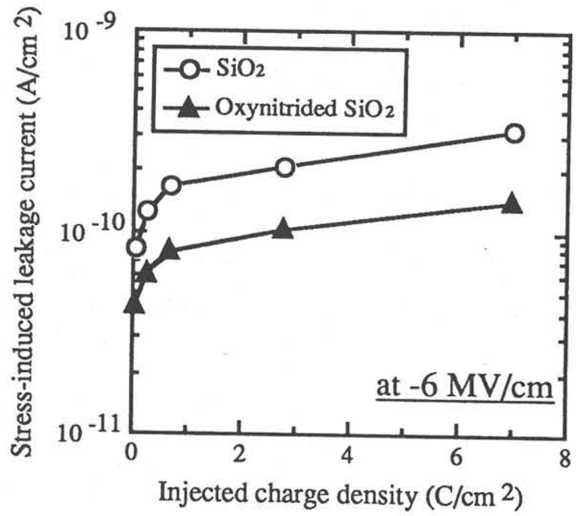

Fig. 5 Stress-induced leakage-current suppression by oxynitridation

is bigger in pyrogenic SiO_2 than in oxynitrided SiO_2, meaning that more holes are trapped in pyrogenic SiO_2. The difference in the current decrease after saturation shows that more electrons are trapped in pyrogenic SiO_2 than in oxynitrided SiO_2 when under Fowler-Nordheim current stress.

After constant current (-10 mA/cm^2) stress, the flatband voltage shifts to a negative (Fig. 3). This means that holes are trapped near the tunnel oxide/Si substrate interface. After 3-C/cm^2 injection, the flatband voltage of the pyrogenic SiO_2 capacitors begins to shift to a positive, indicating that electron trapping does have an influence. The hole and electron trapping corresponds to the leakage current variance shown in Fig. 2. The shift in the flatband voltage is smaller in oxynitrided SiO_2 than in pyrogenic SiO_2. In flash memory, hot holes are injected from the drain side to the tunnel oxide by band-to-band tunneling when electrons are ejected from a floating gate. Therefore, a stronger resistance of oxynitrided SiO_2 to injected holes is the key to improving programming endurance.

In addition, leakage current at a low voltage and interface states should be suppressed for data retention and data reading, respectively, in flash memories after P/E cycles. After constant current stress, the interface-state increase and stress-induced leakage current at -6 MV/cm are dependent on the injected charge (Figs. 4 and 5). Both are suppressed by oxynitridation.

By using a conventional furnace for N_2O oxynitridation, the resistance to high electric-field stress becomes stronger. To clarify the mechanism of improved resistance by oxynitridation, we observed pyrogenic SiO_2 and oxynitrided SiO_2 by XANES (X-ray Absorption Near Edge Structure) analysis. The results show 1.839

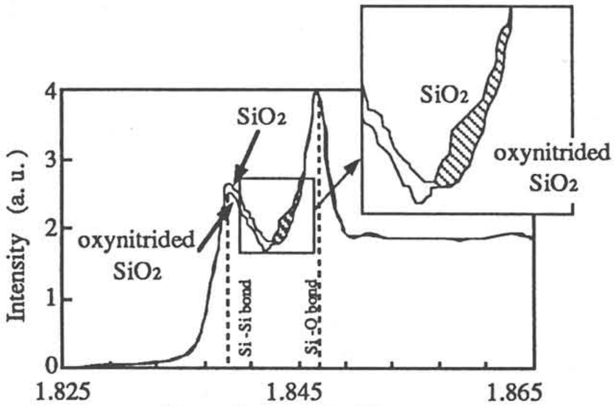

Fig. 6 Tunnel Oxide Structure Analyzed by XANES

unstable bond

$$\equiv Si - \boxed{O - Si} \equiv + \; h^{+} \longrightarrow \; \equiv Si - O^{\bullet} + Si^{+}$$

$$\equiv Si^{+} \; + e^{-} \longrightarrow \; \equiv Si^{\bullet}$$

$$\equiv Si^{\bullet} \; + e^{-} \longrightarrow \; \equiv Si\!:^{-}$$

$$\equiv Si - O^{\bullet} + e^{-} \longrightarrow \; \equiv Si - O\!:^{-}$$

Fig. 7 The model of Fowler-Nordheim stress degradation

keV for the Si-Si bond in the Si substrate and 1.847 keV for the Si-O bond in the SiO_2 films (Fig. 6). For comparison, the Si-O peaks of both oxides are fitted. The difference in the Si-Si peak height is due to the difference in oxide thickness. It is noted that pyrogenic SiO_2 has the shoulder of a Si-O bond peak, and that oxynitrided SiO_2 has no shoulder. The shoulder is thought to denote unstable Si-O bonds which break more easily and generate traps when holes and electrons are injected into a tunnel oxide under high electric-field stress. As shown in Fig. 7, unstable Si-O bonds trap injected holes, separating into $O^{\cdot}$ and Si^{+}. Si^{+} causes the initial increase in the Fowler-Nordheim current as well as the flatband voltage shift to a negative. In the next step, the Si^{+} trapping an electron is converted into $Si^{\cdot}$. Finally, the $Si^{\cdot}$ and $Si\text{-}O^{\cdot}$ trapping an electron converts into $Si\!:^{-}$ and $Si\text{-}O\!:^{-}$. These negatively charged states cause the current to decrease and the flatband voltage to shift to a positive.

As a result of N_2O oxynitridation, the ratio of programming time to the initial programming time is three

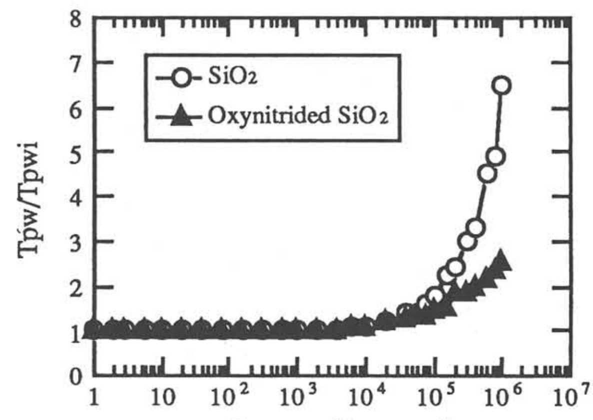

Fig. 8 Programming time improvement by oxynitridation

times smaller in N_2O-oxynitrided SiO_2 than in pyrogenic SiO_2 at 10^6 P/E cycles (Fig. 8). The erasing time is almost the same as the initial value before P/E cycles in both pyrogenic SiO_2 and N_2O-oxynitrided SiO_2. This confirms cycling of up to 10^6 in flash memory.

In conclusion, cycling of up to 10^6 is achieved in a flash memory cell by using N_2O-oxynitrided SiO_2 as the tunnel oxide. This improvement is explained by the fact that N_2O-oxynitrided SiO_2 generates less electron and hole traps under high electric-field stress. The stronger resistance to high electric-field stress is shown to be due to the presence of fewer unstable Si-O bonds, as clarified by XANES analysis.

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