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Relationship between Nitrogen Profile and Reliability of Heavily Oxynitrided Tunnel Oxide Films for Flash EEPROMs

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Higher charge-to-breakdown value (> 110 C/cm^2) and much less threshold voltage narrowing (< 19 %) of the endurance properties for flash EEPROMs was achieved by incorporation of higher nitrogen concentration (~ 10^{21} atoms/cm^3) not only near the oxide/Si interface but also into the bulk of thin oxide films, due to suppression of charge traps. These films were obtained under an optimized heavy oxynitride condition (dry oxidation at 1100 °C; NH_3 anneal at 1000 °C for 30 s; N_2O anneal at 1100 °C for 30 s).

1. Introduction

Highly reliable ultrathin (<12 nm) SiO_2 films are urgently required for advanced nonvolatile memories, such as EPROMs, EEPROMs and flash memories. In scaling down the devices, one of the serious problems is degradation of the tunnel oxide film due to program/erase cycle stress, resulting in narrowing of the threshold voltage (V_t) window and reduction of data retention. Whereas the program/erase cycles are required to be larger than 10^6 repetitions, high-field stress (>8 MV/cm) is applied to the tunnel oxide film during the program/erase cycle. Injection of channel hot electrons or Fowler-Nordheim electrons into the floating gate can cause electron trap and/or hole generation in the tunnel oxide films during the programming operation. Furthermore, holes are injected into the tunnel oxide film by the band-to-band tunneling during the erase mode,[1)] which also degrades the tunnel oxide film. To improve the oxide quality, we have proposed rapid thermal oxynitrided tunnel oxide (RTONO) film formation using a rapid thermal oxidation (RTO)-rapid thermal NH_3 nitridation (RTN)-rapid thermal N_2O oxynitridation (RTON) sequence.[2-4)] This RTONO film shows higher charge-to-breakdown and smaller window closure of the endurance property for flash EEPROMs as compared to pure SiO_2 films. This paper presents the optimum conditions of the RTONO tunnel oxide formation process for realizing high-performance scaled flash EEPROMs.

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2. Experimental

Flash-EEPROM cells with 11-nm-thick tunnel oxide formed by RTO and RTONO were fabricated by means of a 1.4 μm self-aligned stacked gate process. Table 1 shows the tunnel oxide formation process sequences. The inter-poly-ONO film thickness was fixed at 20 nm. To examine the oxide reliability, MOS capacitors were fabricated by depositing n$^+$-poly silicon films, followed by delineating the poly silicon films to have an area of 2×10^{-4} cm^2 on the oxide films. The MOS capacitors were evaluated by high-frequency (1 MHz) capacitance-voltage measurement. Furthermore, the depth profiles of nitrogen (N), hydrogen (H) and oxygen (O) atoms in the oxide films were determined by secondary ion mass spectroscopy (SIMS) using Cs$^+$ as primary ions. The endurance characteristics of flash-EEPROM cells were also evaluated. Programming and erase were performed using channel hot electrons at the drain side and Fowler-Nordheim-tunneling electrons at the source side, respectively.

Table 1 Oxide film formation conditions

	RTO		RTN		RTON
RTO	dry O_2, 1100 °C		-		-
RTONO1	dry O_2, 1100 °C	→	NH_3, 800 °C, 30 s	→	N_2O, 1100 °C, 30 s
RTONO2	dry O_2, 1100 °C	→	NH_3, 900 °C, 30 s	→	N_2O, 1100 °C, 30 s
RTONO3	dry O_2, 1100 °C	→	NH_3, 1000 °C, 30 s	→	N_2O, 1100 °C, 30 s

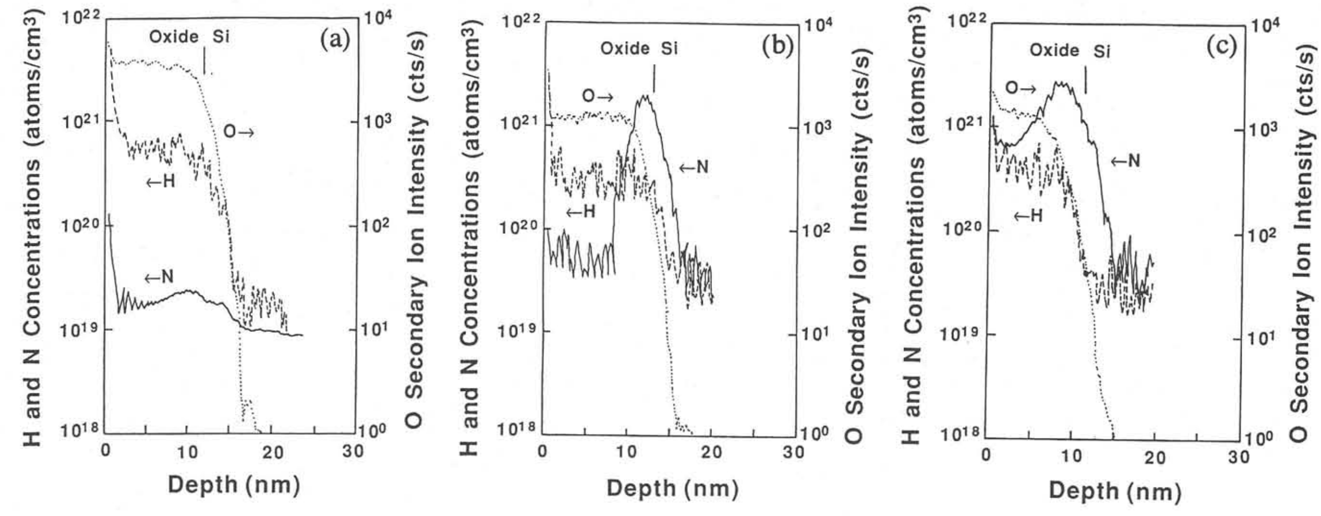

Fig. 1. Depth profiles of N and H atom concentrations, and O atom secondary ion intensities in (a) RTO, (b) RTONO2 and (c) RTONO3 films.

3. Results and Discussion

Figure 1 shows the N, H and O atom depth profiles in the RTO, RTONO2 and RTONO3 films. In the RTONO films, over 10^{21} atoms/cm^3 of N atoms are piled up at the oxide/Si interface and distributed in the bulk oxide. It should be noted that in the RTONO3 film, N atoms beyond 7×10^{20} atoms/cm^3 diffuse into the oxide bulk as well as at the oxide/Si interface. In addition, the concentration of H and O atoms near the oxide/Si interface are decreased by the RTONO process, markedly by the RTONO3 process. Fourier transform infrared spectroscopy-attenuated total reflectance results indicated that [OH] concentration in the RTONO films was much smaller than that in the RTO film (not shown). The H and OH atoms can be included during the RTO and the RTN processes. On the contrary, the N atoms can be incorporated by the RTN and the RTON processes. These findings imply that OH and/or H species in the oxide films are replaced by N atoms during the RTONO process, in particular, in high-temperature RTN and RTON processes.

Fig. 2 shows time-dependent dielectric breakdown (TDDB) characteristics of the RTO, RTONO1, RTONO2 and RTONO3 films. The TDDB characteristics were successfully improved by the RTONO process, as compared to the RTO process. In particular, time-to-breakdown for the RTONO3 film is longer than those for the RTONO1 and RTONO2 films. The flat band voltage shifts (ΔV_{fb}) as a function of injected charge are shown in Fig. 3. ΔV_{fb} for the RTO

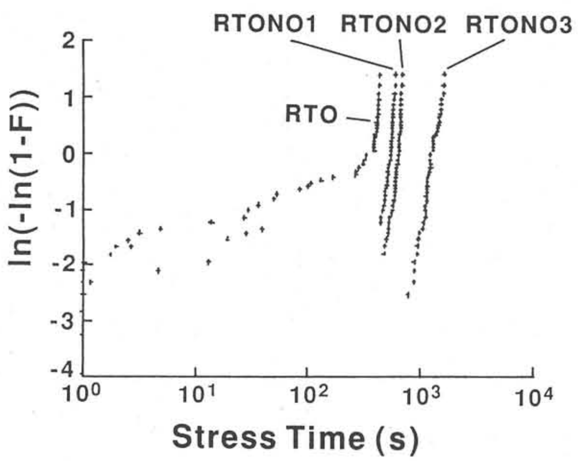

Fig. 2. TDDB characteristics for RTO, RTONO1, RTONO2 and RTONO3 films under constant current stress of 0.1 A/cm^2. Electrons were injected from the substrates to the oxides.

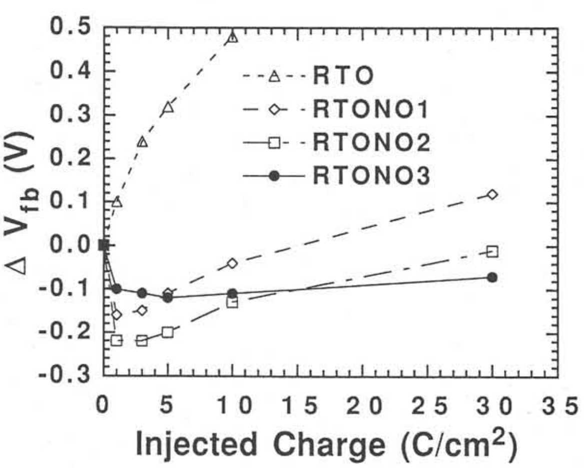

Fig. 3. ΔV_{fb} as a function of injected charge for RTO, RTONO2 and RTONO3 films. The injection current density was 0.1 A/cm^2. Electrons were injected from the substrates to the oxides.

film increased with increasing injected charge. This behavior implies that electron traps are dominant. In contrast, ΔV_{fb} for the RTONO2 and RTONO3 films decreases at initial stages, and gradually increases thereafter. This is explained by hole generation and subsequent electron trap formation. The hole generation may be due to N atoms in the RTONO films. It is noted that ΔV_{fb} for the RTONO3 film is much smaller than those for the RTO and RTONO2 films. Smaller ΔV_{fb} means the suppression of both hole and electron trap generation. We assume that a large amount of N atoms reduces the concentrations of H and OH species in the oxide film, which are possible origins of charge traps, resulting in a longer time-to-breakdown in the TDDB characteristics.

Fig. 4 shows Q_{bd} as a function of N concentration in the bulk oxide ([N]) and at the oxide/Si interface ($[N_{int}]$) for the RTO and RTONO films. The Q_{bd} value of the RTONO3 film (about 120 C/cm^2) was 4 times higher than that of the RTO film. Moreover, it should be noted that Q_{bd} strongly depends on the N profile in the oxide film. While the Q_{bd} value increased with the increase in $[N_{int}]$, Q_{bd} is independent of $[N_{int}]$ when Q_{bd} is higher than approximately 50 C/cm^2. In contrast, it is worth pointing out that Q_{bd} increases with increasing [N] in the bulk oxide. these results strongly suggest that the reliability of the tunnel oxide is improved by introducing N atoms into the bulk oxide as well as at the oxide/Si interface.

Fig. 5 shows the endurance characteristics of flash-EEPROM cells with RTO, RTONO2 and RTONO3 films under accelerated bias conditions. V_t narrowing of the RTONO2 film is 28 %, much smaller than the 70 % of the RTO film after 5×10^4 program/erase cycles. In particular, V_t narrowing less of than 19 % is achieved in the flash EEPROMs using the RTONO3 film . This is considered to be due to incorporation of higher N atoms in the oxide bulk and the oxide/Si interface, reducing charge traps, and resulting in larger Qbd of the RTONO film.

4. Conclusions

Higher Q_{bd} (>110 C/cm^2) and much less V_t narrowing (<19%) of the endurance property for the flash EEPROMs with the RTONO film can be achieved under optimized conditions (RTO at 1100 °C, RTN at 1000 °C for 30 s and RTON at 1100 °C for 30 s), owing to suppression of charge traps by incorporation of a higher concentration of N atoms ($\sim10^{21}$ atoms/cm^3) not only near the oxide/Si interface but also into the bulk of the oxide. Thus, this technology is a key to providing flash EEPROMs in the submicron regime.

Acknowledgments

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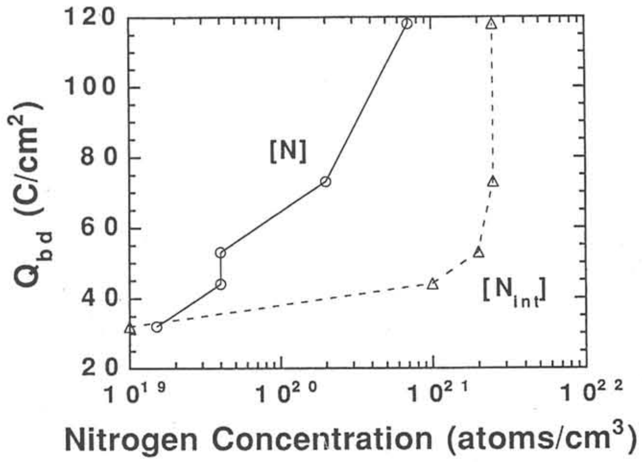

Fig. 4. Q_{bd} (50 % cumulative failure) as a function of nitrogen atom concentration ([N]) at the depth of 4 nm from the oxide surface and at the oxide/Si interface ($[N_{int}]$). Q_{bd}, [N] and $[N_{int}]$ for an RTO film and four RTONO films are plotted.

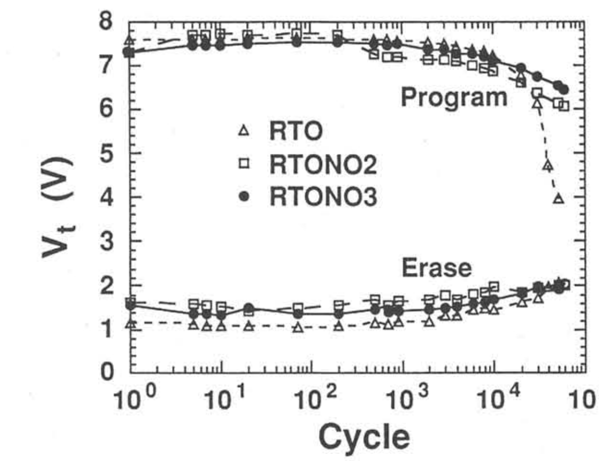

Fig. 5. Endurance characteristics of flash-EEPROM cells using RTO, RTONO2 and RTONO3 films. Gate length and width are 1.4 μm and 0.7 μm, respectively.
program: drain bias, 7 V; control gate bias, 13 V.
erase: source bias, 12 V; control gate bias, 0.