Effect of Nitrogen Profile on Tunnel Oxynitride Degradation with Charge Injection Polarity

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The relationship between nitrogen profiles and polarity dependence of wearout and breakdown in oxynitiride films has been investigated. With positive bias stress, nitrogen atoms at the oxide/Si interface suppress charge trap and interface state generation, and produce larger charge-to-breakdown (Q_{bd}) . In contrast, with negative bias stress, the interface nitrogen atoms decrease charge traps, however, cannot reduce interface state generation and thus give smaller Q_{bd} . Furthermore, nitrogen atoms of the oxide surface cause undesirable results for both bias stresses.

1. INTRODUCTION

The improvement of tunnel oxide film reliability is one of the key issues of advanced flash electrically erasable and programmable read only memory (EEPROM) development. In flash EEPROMs, electrons are injected into a floating gate and ejected from the floating gate through the tunnel oxide film during programming and erasing operations, using Fowler-Nordheim tunneling or channel hot electrons. The program/erase cycles are required to be greater than 10⁶ repetitions, in addition, high-field stress of greater than 10 MV/cm is applied to the tunnel oxide film during programming and erasing operations. Thus, it is important to investigate the reliability of thin oxide films under negative as well as positive gate bias stress. Several authors have reported the polarity dependence of thin oxide film degradation.¹⁻⁵) It has been found that the time-dependent dielectric breakdown (TDDB) lifetime for positive bias stress is longer than that for negative bias stress, and TDDB lifetimes for both bias stress depend on the oxide thickness.^{1, 2, 5} Moreover, it has been pointed out that the asymmetry of the charge-tobreakdown (Q_{bd}) due to charge injection polarity is reflected in the evolution of interface state generation.⁴⁾ On the contrary, the wearout of oxide films has been reported to be independent of stress polarity, although the breakdown depended on the stress polarity.³⁾

However, little information on the relationship between nitrogen profile and polarity dependence of oxynitride film degradation has been obtained, while oxynitride films are appropriate for use as tunnel oxide films.^{6, 7)} In this paper, we will discuss the effect of the nitrogen concentration profile in thin oxynitride films upon bias polarity dependence of wearout and breakdown.

2. EXPERIMENTAL

Oxynitride (NO, $ONN^{6,7)}$, ONO) and dry oxide (RTO) films were formed on n-type and p-type Si wafers by process as shown in Table I. Little difference of oxide breakdown characteristics between n-type and p-type wafers has been reported.¹) The film thickness was about 9 nm. N⁺-polysilicon films were deposited on the films as electrodes. Constant current stress of 10.11 A/cm^2 was applied to the MOS capacitors under the accumulation mode. The interface state density (D_{it}) at the mid gap was derived from the high-frequency (1 MHz) and the quasistatic capacitance-voltage methods. The depth profiles of nitrogen, hydrogen and oxygen atom concentrations in the films were determined by secondary ion mass spectroscopy (SIMS) using Cs⁺ as primary ions at 1 keV.

Table I. Sample preparation conditions

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Sample	RTO (dry O ₂)	RTN (NH ₃)	RTO (dry O ₂)	RTON (N ₂ O)
RTO	1100 °C, 30 sec	-	-	-
NO	1100 °C, 19 sec	1. 	-	\rightarrow 1100 °C, 30 sec
ONN	1100 °C, 23 sec	→ 1000 °C, 30 sec	-	\rightarrow 1100 °C, 30 sec
ONO	1100 °C, 25 sec	\rightarrow 1000 °C, 30 sec	\rightarrow 1100 °C, 30 sec	



Fig. 1. Nitrogen (N), hydrogen (H) and oxygen (O) atom concentration depth profiles in (a) RTO, (b) NO, (c) ONN and (d) ONO.

3. RESULTS AND DISCUSSION

Figs.1 (a)-(d) show nitrogen, hydrogen and oxygen atom concentrations determined by SIMS in RTO, NO, ONN and ONO, respectively. Nitrogen atoms of 0.8 at.% accumulate near the oxide/Si interface of NO. Moreover, in ONN and ONO, a greater amount of nitrogen atoms (2.1 at.%) is accumulated near the oxide/Si interface, and distributed in the oxide bulk. In addition, it should be noted that surface nitrogen atom concentration of ONN (< 0.1 at.%) is much less than that of ONO (> 1.5 at.%). Here, nitrogen atoms below 1 nm in depth do not show ones in the films but ones absorbed on the film surface in Figs. 1. Little difference between hydrogen and oxygen atom concentration profiles among the samples is observed.

Fig. 2 shows the TDDB characteristics of RTO, NO, ONN and ONO with positive and negative bias stress. With positive bias stress, Q_{bd} (50 % cumulative failure) increases in the order of RTO, NO, ONO and ONN. In contrast, Q_{bd} with negative bias stress is much smaller than that with positive bias stress. Moreover, the difference in Q_{bd} among the samples is also much less than that in Q_{bd} among the samples with positive bias stress, while Q_{bd} slightly decreases in the order of NO, RTO, ONN and ONO.

The gate voltage shift (ΔV_g) of the samples as a function of injected charge is shown in Figs. 3 (a) and (b). With negative bias stress, ΔV_g of RTO abruptly decreases at the initial stage of the stress, and increases thereafter. This indicates that hole trap formation at the initial stage and subsequent electron trap formation are dominant. On the contrary, in case of NO, ONN and ONO, electron trap formation is dominant at the initial stage, and is saturated thereafter. In particular, electron traps abruptly cause at the initial stage in case of ONO. Moreover, ΔV_g of NO and ONN is reduced, compared to RTO and ONO. These findings strongly suggest that the incorporation of nitrogen at the oxide/Si interface suppress both initial hole trap and subsequent electron trap formation; however, surface nitrogen atoms in ONO form initial abrupt electron traps with negative bias stress. In contrast, with positive bias stress, electron traps decrease in the order of RTO, NO, ONO and ONN, while hole traps are slightly formed at the initial stage (Fig. 3 (b)). These results indicate that



Fig. 2. TDDB characteristics of RTO, NO, ONN and ONO with negative and positive bias stress of |0.1| A/cm².



Fig. 3. Gate voltage shift (Δ V_g) as a function of injected charge in RTO, NO, ONN and ONO with (a) negative and (b) positive bias stress of 10.11 A/cm².

electron trap formation is successfully suppressed by introduction of higher nitrogen atom concentration at the oxide/Si interface in case of positive bias stress.

Little difference in the increase of Dit among all samples is observed with negative bias stress, as shown in Fig.4 (a). This is because the increase in Dit is mostly determined due to the primary damage caused by electrons injected into the oxide/Si interface, and by the release of hydrogen-related and/or holes at the oxide/Si interface in case of negative bias stress. The great primary damage can make Dit generation be independent of the nitrogen profile. In contrast, with positive bias stress (Fig.4 (b)), the increase in D_{it} of NO, ONN and ONO, in which nitrogen atoms are included at the oxide/Si interface is smaller than that in Dit of RTO. In particular, the increase in Dit of ONN is reduced. These are because in case of the positive bias stress, Dit is mainly increased due to secondary damage induced by hydrogen-related and/or holes released from the polysilicon/oxide interface. The interface nitrogen atoms can decrease the secondary damage caused by the hydrogen-related and/or holes. However, it implies that surface nitrogen atoms increase Dit.

We believe that a larger amount of nitrogen atoms near the oxide/Si interface reconstructs the structural transition layer near the oxide/Si interface, which can become the source of charge traps and Dit generation. Therefore, the interface nitrogen atoms can suppress charge traps and D_{it} generation induced by hydrogen-related and/or holes, resulting in larger Qbd. However, surface nitrogen atoms may become excess nitrogen atoms in the oxide film. Thus, the excess surface nitrogen atoms change mechanical stress in the oxide film, increasing charge traps and Dit. Consequently, the breakdown and the wearout with positive bias stress are improved by introduction of nitrogen atoms at the oxide/Si interface. However, the introduction of nitrogen atoms into an oxide film, RTO, can not provide successful improvement for negative bias stress, since the degradation with negative bias stress in RTO is much greater than that with positive bias stress.

4. SUMMARY

The incorporation of higher nitrogen concentration (2.1 atm.%) at the oxide/Si interface suppresses charge trap formation and D_{it} generation, and produces larger Q_{bd} with positive gate bias stress. In contrast, with negative gate bias stress, the incorporation of nitrogen atoms at the oxide/Si interface decreases charge traps, however, cannot reduce D_{it} generation, and hence gives smaller Q_{bd} . Moreover, with both positive and negative gate bias stresses, higher surface nitrogen atom concentration (>1.5 atm.%) gives negative effect on a decrease in charge traps, D_{it} generation and an increase in Q_{bd} . As a result, ONN process (RTO - RTN - RTON (N₂O)) successfully increases the interface nitrogen concentration, and thus produces highly reliable tunnel oxide films.

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Fig. 4. D_{it} at the mid gap as a function of injected charge of RTO, NO, ONN and ONO with (a) negative and (b) positive bias stress of I0.11 A/cm².