Extended Abstracts of the 1992 International Conference on Solid State Devices and Materials, Tsukuba, 1992, pp. 425-427

PD3-2

Novel Single-Step Oxynitridation (SS-RTON) Technology for Forming Highly Reliable EEPROM Tunnel Oxide Films

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We have proposed a novel single-step oxynitridation (SS-RTON) technology to obtain highly reliable ultrathin EEPROM tunnel oxide films. The SS-RTON process can be achieved by rapid switching of the ambient gases ($O_2 \rightarrow N_2O$) at the midpoint of the oxidation time, maintaining the oxidation temperature. The results indicated almost no increase in the oxide-trap-assisted leakage and/or in the electron trap density, resulting in the increase of the charge-to-breakdown. Moreover, it has been clarified from SIMS measurement that a large number of N atoms (10^{22} atoms/cm^3) are incorporated in the film.

1. INTRODUCTION

Highly reliable thin (<10 nm) dielectric films are urgently required for scaled floating-gate memories, such as advanced EPROM's, EEPROM's and flash memories. In the scaling down of the EEPROM tunnel oxide, one of the serious limiting factors is the oxide leakage current induced by write/erase (W/E) cycling stress, resulting in data retention degradation [1-3]. Baglee and Smayling [4] found, for the first time, an increase in leakage current during high-field stress. To date, this conduction has been assumed to be due to the generation of localised defects or weak spots [5], localised positive charges [6], and/or trap sites near the injecting interface [4,7]. However, the mechanism of the conduction is still unclear. We have shown, for the first time, that whatever the origin, the oxide leakage can be decreased in N_2O-oxynitrided (RTON) SiO_2 films [8,9], resulting in an increase of the charge-to-breakdown. Moreover, we have found that in NH_3-nitridation the oxide leakage is strongly dependent on the nitridation time [10]. In addition, it has been clarified that there is a strong correlation between the number of electron traps, the low-field leakage current, and the charge-to-breakdown values. These results indicate that in ultrathin SiO_2, the oxide leakage is a result of trap-assisted tunneling, leading to a breakdown event when a critical trap density is reached. The Si-N bond reduces electron trap density, whereas the N-H bond increases it [8-10].

In this paper, to obtain a further reliable ultrathin EEPROM tunnel oxide film, a novel single-step RTON (SS-RTON) process is introduced for the first time. The effect of SS-RTON on high-field-induced degradation for ultrathin SiO_2 film as compared to those of RTO and RTON films will be demonstrated.

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 [11]. The rapid thermal processing (RTP) apparatus used was equipped with tungsten-halogen lamp heaters and an oil-free high-vacuum pumping system. Table 1 shows the process sequences employed. Three kinds of oxide films have been formed: RTO (#1), RTON (#2) and SS-RTON (#3) SiO_2 films. As Fig.1 shows, the SS-RTON process is achieved by rapid switching of the ambient gases ($O_2 \rightarrow N_2O$) at the midpoint of the oxidation time, maintaining the oxidation temperature. 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 means of I-V and time-dependent dielectric breakdown (TDDB) tests for both polarity bias stresses. Electrons were injected in the Fowler-Nordheim (F-N) tunneling region in order to simulate actual EEPROM device operation. The film composition and its chemical bonds were evaluated by secondary ion mass spectroscopy (SIMS) and X-ray photoelectron spectroscopy (XPS) measurement.

3. RESULTS & DISCUSSION

The gate voltage shifts (ΔV_g) under constant current stress are shown in Fig.2. For positive bias stress, RTO (#1), RTON (#2) and SS-RTON (#3) SiO_2 films all show a V_g decrease at initial stages, followed by almost linear increases. For negative stress, RTO SiO_2 (#1) shows large V_g decrease at the initial stage, as compared to those of RTON (#2) and SS-RTON (#3) films. The initial V_g decrease is attributed to hole generation. In addition, RTO (#1) SiO_2 shows linear increase of the V_g after a local minimum. This means that electron traps are generated during stress. It is noted that although all samples show V_g decreases at the initial stages, the RTON (#2) and SS-RTON (#3) SiO_2 films indicate a much smaller V_g shift than that of pure SiO_2 (#1) film. The dV_g/dQ_{inj} value corresponds to the generation rate of electron traps induced by constant current stress [12]. This result indicates that by N_2O-oxynitridation, bulk electron traps can be greatly reduced in number. For both polarity biases, the electron trap generation rate increases in the order #3, #2 and #1. The charge-to-breakdown (Q_{BD}) of these samples shows the opposite tendency as the dV_g/dQ_{inj} case. That is, the Q_{BD} increases in the order #1, #2 and #3.

Figure 3 shows typical I-V characteristics of 5nm-thick oxide films before and after stressing. Anomalous leakage occurs on the low-field side (<8MV/cm) at both stresses. This behavior is remarkable for RTO SiO_2 (#1), but not so for RTON SiO_2 (#2 & #3). In particular, in the SS-RTON (#3) film, a 70% decrease compared to that of the RTO (#1) film, is achieved. The nature of the low-field conduction is not well understood at this time. However, it does seem to be well fitted by the Fowler-Nordheim type conduction mechanism [13]. Moreover, this new finding is closely related to the small V_g shift of SS-RTON SiO_2, that is, it seems to be connected with the low rate of electron trap generation, as shown in Fig.2. This result can also be explained in terms of the idea that N atoms piled up at the SiO_2/Si interface reduce the trap sites [9].

The process dependence on the TDDB characteristics for the SS-RTON is shown in Fig.4. For ultrathin SiO_2 film, it is important to improve the $Q_{BD}(-)$ in the ultrathin regime [9]. In the RTO (#1) SiO_2 film, $Q_{BD}(-)$ is typically 5 C/cm^2. In contrast, SS-RTON (#3) SiO_2 film shows that with increasing SS-RTON time $Q_{BD}(-)$ increases in proportion to SS-RTON time. When optimum N_2O-time is chosen, the $Q_{BD}(-)$ reaches 20 C/cm^2, which corresponds to that of 9-nm-thick SiO_2 film [9]. Moreover, the $Q_{BD}(+)$ value also increases to 200 C/cm^2. It can be assumed that a large $Q_{BD}(-)$ value, and much

Table 1. Preparation sequences employed in this study.

No.	Tox	RTO	RTON
#1	5nm	O_2, 1100℃, 10s	
#2	5nm	O_2, 1100℃, 1s →	N_2O, 1100℃, 30s
#3	5nm	O_2, 1100℃, 4s/N_2O, 950℃, 5-180s	

#1:RTO, #2:RTON, #3:SS-RTON

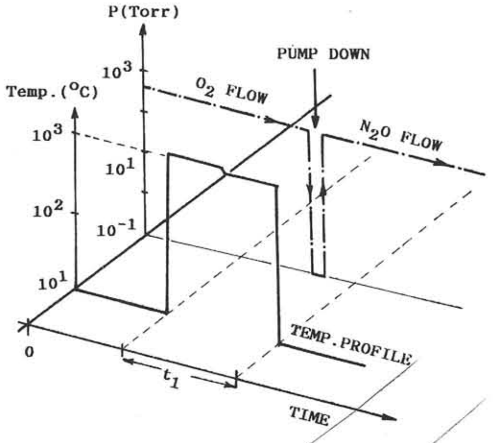

Fig.1 Temperature and gas flow profiles for SS-RTON process.

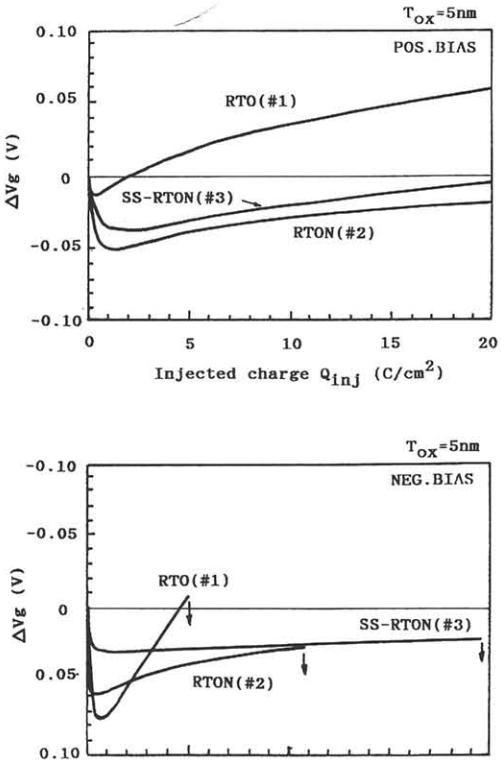

Fig.2 Gate voltage shifts against injected charge for samples (#1)-(#3) @J_{OX}= ±100mA/cm^2.

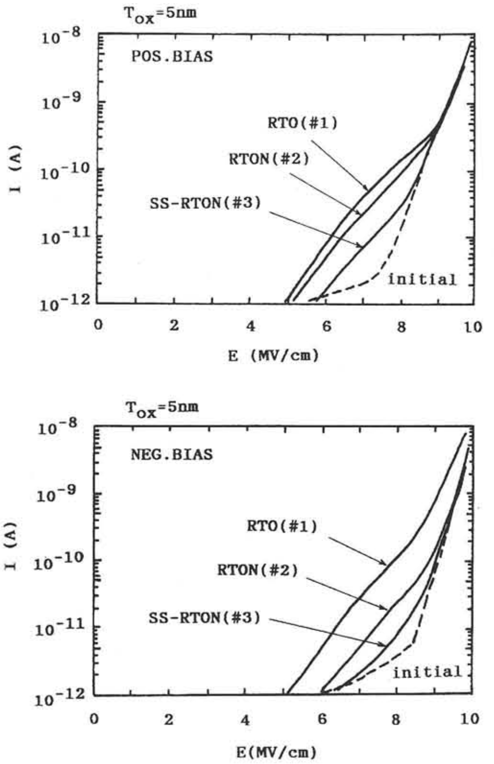

Fig.3 Leakage currents through samples (#1)-(#3) @Q_{inj}=5C/cm^2.

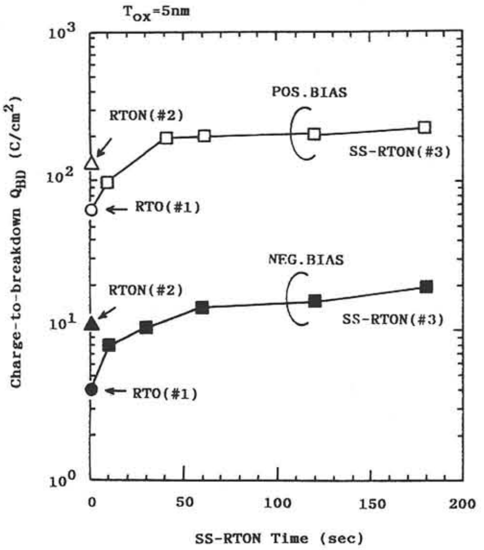

Fig.4 The dependence of SS-RTON time on the charge-to-breakdown.

smaller leakage current and electron trap density of SS-RTON SiO_2 film is strongly related to the number of N atoms in bulk SiO_2.

The depth profiles of N atoms by SIMS measurements are shown in Fig.5. As anticipated, a large number of N atoms were observed in bulk SiO_2 in the SS-RTON (#3) SiO_2 films. This indicated that in the SS-RTON process, strong Si-N bonds, which are evaluated by XPS (not shown), are formed.

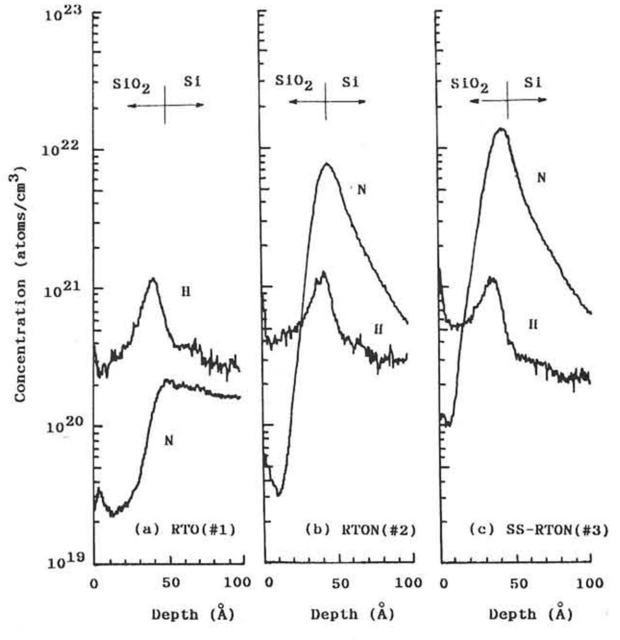

Fig.5 SIMS depth profiles of N and H atoms in samples (#1)-(#3).

4. CONCLUSIONS

Review of the data suggests that the strong SiN bond (4.6 eV) forms a small capture cross section of electron traps for injecting electrons, resulting in almost no increase in the oxide trap-assisted leakage or in the increase of the charge-to-breakdown. In particular, the single-step oxynitridation (SS-RTON) process is more effective for improving the oxide quality, because large amounts of nitrogen are incorporated. Thus, the SS-RTON technology proposed provides a breakthrough in the EEPROM tunnel oxide thickness limitation.

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