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Role of SiN Bond Formed by N_2O-Oxynitridation for Improving Dielectric Properties of Ultrathin SiO_2 Films

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Dielectric properties of rapid-thermally N_2O-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_2O as reactants [9-11], and succesfully applied it to the gate oxide of sub-halfmicron CMOSFETs [12]. In this paper, the dielectric properties of N_2O-oxynitrided ultrathin SiO_2 films will be demonstrated. Then, the role of SiN bond formed by this N_2O-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 toal 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

stress are shown in Fig.1. In both polarity biases, N_2O-oxynitrided (RTON) SiO_2 (#3) showed much smaller V_g shifts as compared to those of RTO SiO_2 (#1) and NH_3-nitrided (RTN) SiO_2 (#2). The V_g shift occurs when electrons are trapped in the film, maintaining a constant field at the injecting interface [14,15]. The dV_g/dt value also corresponds to the generation rate 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 (Q_{BD}) for samples #1-#4. For positive bias stress, $Q_{BD}(+)$ increased with decreasing oxide film thickness. In the oxide thickness region of 5 -6nm, RTON SiO_2 films (#3 & #4) have larger $Q_{BD}(+)$ 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, $Q_{BD}(-)$ generally decreases as thinning oxide film thickness. However, only the $Q_{BD}(-)$ value for RTON SiO_2 (#3) seems to be slightly higher than those of samples #1, #2 and #4. As for a lower $Q_{BD}(-)$ value in RTON SiO_2 (#4), the reason is still unclear. One explanation is that the local field enhancement due to the SiO_2/Si interface roughness and/or oxide thickness inhomogeneity causes lower $Q_{BD}(-)$ value [10]. As thinning oxide film thickness, low-field leakage through SiO_2 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 the 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 RTN SiO_2 (#2), but not for RTON SiO_2 (#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 N_2O-oxynitridation, 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 SiO_2/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 SiO_2(#1), N atoms are not observed in the bulk and/or at the SiO_2/Si interface within detection limits. On the contrary, for samples #2-#4, an accumulation of N atoms was

Table 1. Preparation sequences of N_2O-oxynitrided, pure SiO_2 and NH_3-nitrided SiO_2 films.

No.	T_{ox}	RTO	RTON (RTN)
#1	6-10nm	O_2,1100°C,4-30s	
#2	6-10	O_2,1100°C,4-30s →	NH_3,1000°C,30s
#3	6-10	O_2,1100°C,2-12s →	N_2O,1100°C,4-34s
#4	5-6	--------	N_2O,1100°C,28-40s

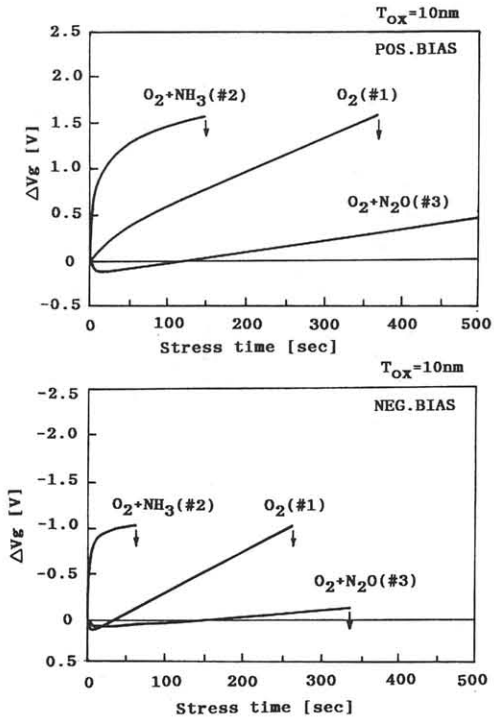

Fig.1 Gate voltage shift (ΔV_g) as a function of stress time. @J_{ox}= ±100mA/cm^2.

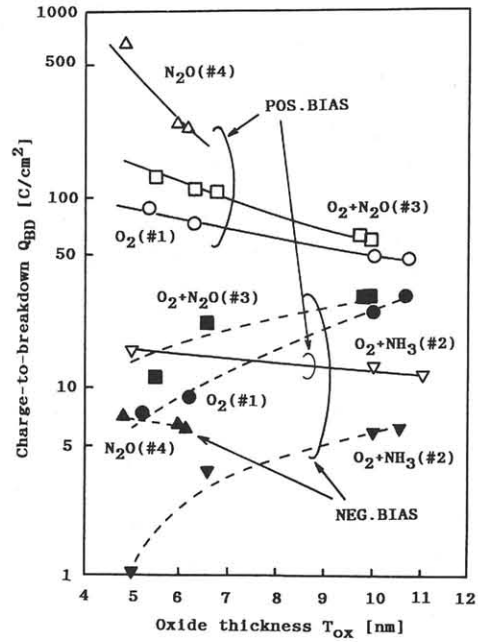

Fig.2 Oxide film thickness dependence of charge-to-breakdown (Q_{BD}) under the same stress condition. @J_{ox}= ±100mA/cm^2.

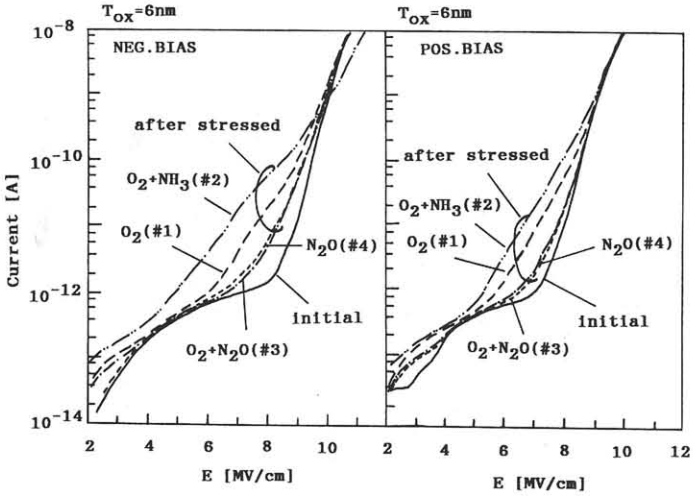

Fig.3 Leakage current through 6nm-thick oxide films (#1-#4) before and after charge injection stress, @Q_{inj}=1C/cm^2 at J_{ox}= ±100mA/cm^2.

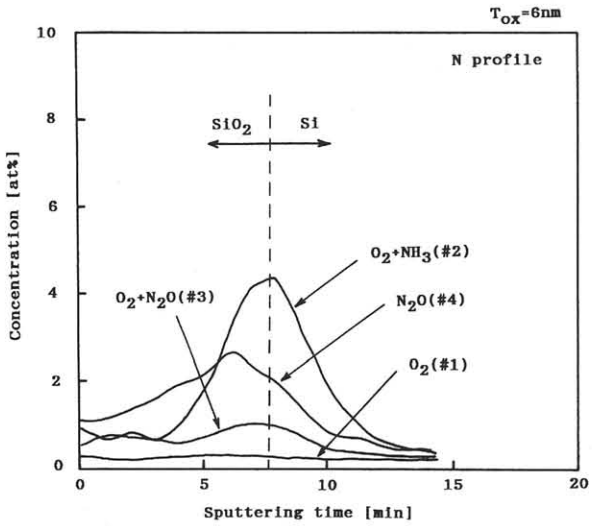

Fig.4 AES depth profiles of N atoms for samples #1-#4.

observed at the SiO_2/Si interface.

The densities of NH, SiH, SiOH and H_2O 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 mode, and are not accesible 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 RTON SiO_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 $O_3 \equiv Si\text{-}H + e^- \rightarrow O_3 \equiv Si^- + H^0$. If these weak H-related species are replaced by Si-N bonds, the electron trapping densities can be be reduced. The electron traps may also induce the conduction via trapping sites and closely related to the high-field induced

Table 2. FT-IR ATR and XPS results for samples #1, #2, #3 and #4.

T_{ox}=6nm

No.	SiOH	H_2O	NH	SiH	SiN
#1	ND	95	ND	ND	ND
#2	ND	137	295	33	290
#3	ND	74	ND	ND	30
#4	0.98	54	ND	ND	120

ND ; not detected (x10^{19}atoms/cm^3)

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 Q_{BD} value.

4. CONCLUSION

we have studied N_2O-oxynitridation for improving dielectric properties of SiO_2 films. By this technology, ultrathin (5-10nm) SiO_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_2O-oxynitrided SiO_2 film are originated from strong Si-N bond formation in the SiO_2 film.

REFERENCES

[1] K.Naruke,S.Taguchi and M.Wada : IEEE IEDM Tech.Dig.,pp.424 (1988).
[2] K.Yoshikawa,S.Mori,E.Sakagami,N.Arai, Y.Kaneko and Y.Ohshima : IEEE VLSI Symp. Tech.Dig.,pp.79 (1991).
[3] T.Ito,T.Nakamura and H.Ishikawa : IEEE Trans.Electron Devices,**ED-29** (1982)498.
[4] H.H.Tsai,L.C.Wu,C.Y.Wu and C.Hu : IEEE Electron Device Lett.,**EDL-8** (1987) 143.
[5] P.Pan : J.Appl.Phys.,**61** (1987) 284.
[6] S.K.Lai,J.Lee and V.K.Dham : IEEE IEDM Tech.Dig.,pp.190 (1983).
[7] T.Hori,H.Iwasaki and K.Tsuji : IEEE Trans.Electron Devices,**36** (1989) 340.
[8] N.Novkovski,M.Dutoit,J.S.Zaldivar : Appl.Phys.Lett.,**56** (1990) 2120.
[9] H.Fukuda,T.Arakawa and S.Ohno : IEE Electronics Lett.,**26** (1990) 1505.
[10] H.Fukuda,T.Arakawa and S.Ohno : Extended Abstracts 22nd Conf.SSDM (1990)pp.159.
[11] H.Fukuda,M.Yasuda and S.Ohno : IEE Electronics Lett.,**27** (1991) 440.
[12] A.Uchiyama,H.Fukuda,T.Hayashi,T.Iwabuchi, and S.Ohno : IEEE IEDM Tech.Dig.,(1990) pp.425.
[13] H.Fukuda,A.Uchiyama,T.Hayashi,T.Iwabuchi and S.Ohno : Jpn.J.Appl.Phys.,**29** (1990) L137.
[14] M.S.Liang and C.Hu : IEEE IEDM Tech. Dig., (1981) pp.396.
[15] C.F.Chen,C.Y.Wu,M.K.Lee and C.N.Chen : IEEE Trans.Electron Devices,**ED-34** (1987) 1540.