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Effects of NH₃ nitridation on oxides grown in pure N₂O ambient

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Effects of NH₃ nitridation on the chemical and electrical properties of N₂O oxides have been studied. Compared with NH₃-nitrided SiO₂, NH₃ nitridation does not degrade the electrical properties of N₂O oxides, thus resulting in superior impurity diffusion barrier properties, while preserving excellent interface immunity to hot-carrier injection and much lower charge trapping. Correlation studies between the chemical and electrical properties of NH₃-nitrided N₂O and NH₃-nitrided SiO₂ have been done to explain these results.

Oxynitrides have been found to be an attractive replacement for conventional SiO₂ as gate dielectrics. The motivation for using oxynitrides is that the nitrogen incorporated at the gate-oxide/silicon interface strengthens the interface and renders it immune to hot-carrier damages.^{1,2} The other important advantage of incorporating nitrogen is that it acts as a good barrier to boron penetration which comes about when *p*⁺-polysilicon is used in the fabrication of the gate electrode in *p*-type metal-oxide-semiconductor field-effect transistors (*p*-MOSFETs).^{3,4} Due to the high amounts of nitrogen ([N]) at the Si/SiO₂ interface, NH₃-nitrided SiO₂ shows superior boron-stopping properties compared to pure oxides. However, they suffer from hydrogen-related electron trapping, which makes these dielectrics unacceptable for *p*-MOSFET applications.⁵ On the other hand, even though oxynitrides grown by thermal oxidation of Si in N₂O have shown superior electrical properties and reliability,⁶ these dielectrics have low levels of nitrogen.^{7,8} Hence, in order to retain the excellent electrical characteristics and at the same time improve the diffusion barrier properties to boron penetration, one needs to increase the nitrogen levels in N₂O oxides. We have accomplished this by performing NH₃ nitridation of N₂O grown oxides.³ The electrical data presented in Ref. 3 show that NH₃ nitridation of N₂O oxides provides an equally effective boron penetration barrier as NH₃-nitrided SiO₂, without degrading the dielectric reliability properties of the resulting dielectric. In this letter we have used angle resolved x-ray photoelectron spectroscopy (ARXPS) to investigate the chemical modification of the N₂O oxide upon NH₃ nitridation and its correlation with electrical properties. A comparative study of the bonding structures and electrical properties between NH₃-nitrided N₂O oxides and NH₃-nitrided SiO₂ has been done. Compared to NH₃-nitrided SiO₂, NH₃-nitrided N₂O oxides have much higher immunity to hot-carrier damages. The chemical composition of the two dielectrics are also very different. The difference in interface hardness has been attributed to the presence of a N—O bond in N₂O based oxides.

Samples for ARXPS study were prepared by rapid thermal processing (RTP). N₂O oxide was prepared by RTP at 950 °C for 10 s in N₂O ambient and NH₃-nitrided N₂O oxide samples were prepared by RTP of the N₂O oxide at 950 °C

for 20 s in NH₃ ambient. The thickness of the XPS samples was measured to be less than 25 Å. MOS capacitors with *n*⁺-polysilicon gate were used for electrical characterization and were fabricated on a 3–5 Ω cm (100) *p*-type Si substrate. N₂O and O₂ gate oxides were grown at 950 °C by using a conventional resistance-heated furnace. Electrical measurements performed on RTP and furnace-grown gate oxides revealed no significant difference. Some of the N₂O oxides were NH₃-nitrided at 900 °C for different durations (0–20 min). O₂ gate oxides (pure SiO₂) were nitrided at 900 °C for 5 min in NH₃ ambient. All NH₃-nitrided oxides were annealed in N₂ at 950 °C for 20 min. The thicknesses of the gate oxides were measured to be 80 Å.

In order to identify the chemical bonding structure at the interface of various dielectrics, deconvolution of N 1s spectra obtained from ARXPS was performed. Figure 1 shows the deconvolution of N 1s spectra of the N₂O oxide. Two peaks corresponding to Si≡N bond at 397.6 eV (Ref. 9) and Si₂=N—O bond at 399.8 eV (Ref. 10) are observed. Due to the absence of hydrogen in the nitridation ambient, we do not see any evidence of hydrogen-related bonds from the XPS analysis. Deconvolution of N 1s spectra for NH₃-nitrided

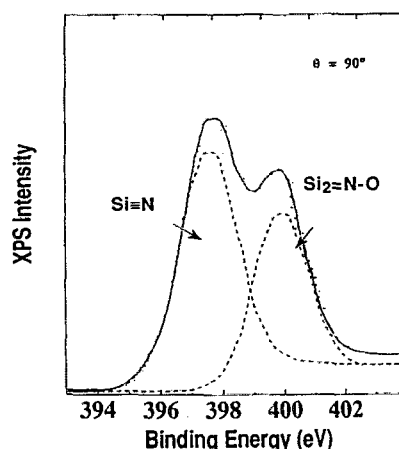


FIG. 1. Deconvolution of N 1s spectra obtained by ARXPS of N₂O oxide at an angle of 90° between the analyzer axis and the plane of the wafer.

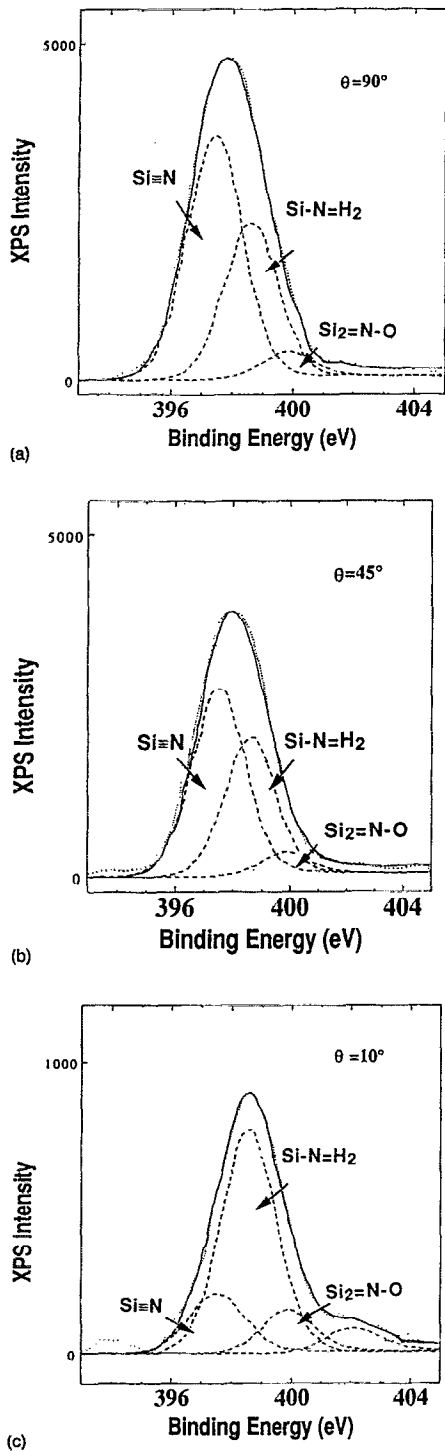


FIG. 2. Deconvolution of N 1s spectra obtained by ARXPS of NH_3 -nitrided N_2O oxide at an angle of (a) 90° , (b) 45° , and (c) 10° between the analyzer axis and the plane of the wafer.

N_2O oxides shows a peak at a binding energy of 398.6 eV in addition to the $Si\equiv N$ peak and $Si_2=N-O$ peak, throughout the bulk of the oxide [Figs. 2(a)–2(c)]. The peak at 398.6 eV has been identified by Bischoff *et al.* as the position of a silamine group ($Si-N=H_2$).^{11,12} In addition, the intensity of the $Si\equiv N$ peak increases significantly. Deconvolution of N 1s spectra of NH_3 -nitrided SiO_2 (not shown) also shows the presence of the hydrogen-based silamine group ($Si-NH_x$) due

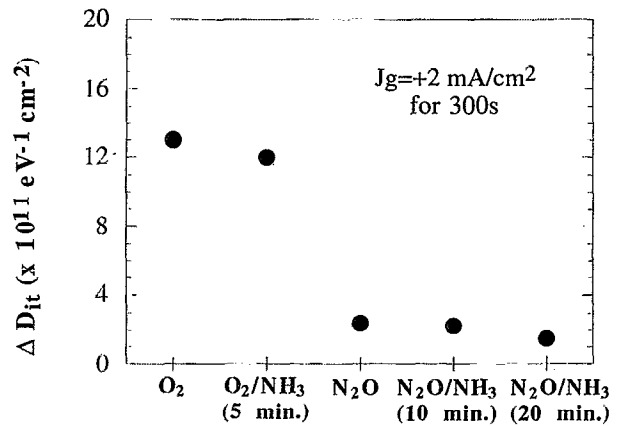


FIG. 3. Midgap interface state density ($\Delta D_{it,m}$) in MOS capacitors with different gate dielectrics caused by Fowler–Nordheim injection of $0.6 C/cm^2$ of charge from the substrate.

to the presence of NH_3 in the nitridation ambient. However, no $Si_2=N-O$ bond, as observed in N_2O -based oxides, is seen in these samples. In the discussion that follows, the significance of the chemical structure as identified above and its relationship to the electrical and reliability properties of the dielectrics will be illustrated.

Figure 3 compares the interface state generation (ΔD_{it}) in pure SiO_2 , NH_3 -nitrided SiO_2 , N_2O oxide, and NH_3 -nitrided N_2O oxides with varying nitridation times under constant current stress (substrate injection) after the injection of $0.6 C/cm^2$ of charge. Results shown in Fig. 3 indicate that varying NH_3 nitridation time of N_2O oxides from 0 to 20 min does not degrade ΔD_{it} after injection of charge. In fact, all N_2O -based oxides, i.e., N_2O oxides and NH_3 -nitrided N_2O oxides with varying nitridation times, show equally good resistance to stress-induced interface state generation. This result is an indication of the fact that even though subsequent nitridation of N_2O in NH_3 ambient increases the intensity of the $Si\equiv N$ bond significantly, it does not enhance the immunity of N_2O oxides to interface state generation. On the other hand, although NH_3 nitridation significantly increases $Si\equiv N$ bonds in SiO_2 , it degrades ΔD_{it} of SiO_2 considerably. Since no $Si_2=N-O$ bond is observed in the XPS analysis of NH_3 -nitrided SiO_2 , these observations indicate that perhaps the $N-O$ bond plays a more important role than the $Si\equiv N$ bond in determining the interface hardness to hot-carrier injection. The absence of the $N-O$ bond in NH_3 -nitrided SiO_2 is probably the main reason for the lack of improvement in the interface quality of SiO_2 upon NH_3 nitridation. The relationship between the presence of $N-O$ bond and the excellent interface quality of N_2O -based samples also provides evidence for the role of the $N-O$ bond in determining immunity to interface state generation. It is also important to bear in mind that the post-nitridation anneal of the NH_3 -nitrided SiO_2 sample used in our experiments is performed in N_2 , unlike NH_3 -nitrided SiO_2 samples annealed in O_2 , popularly known as reoxidized nitrided oxides (ROX-NOX). It has been shown before that NH_3 -nitrided SiO_2 annealed in N_2 shows worse ΔD_{it} properties compared to NH_3 -nitrided SiO_2 annealed in O_2 .¹³ This difference in inter-

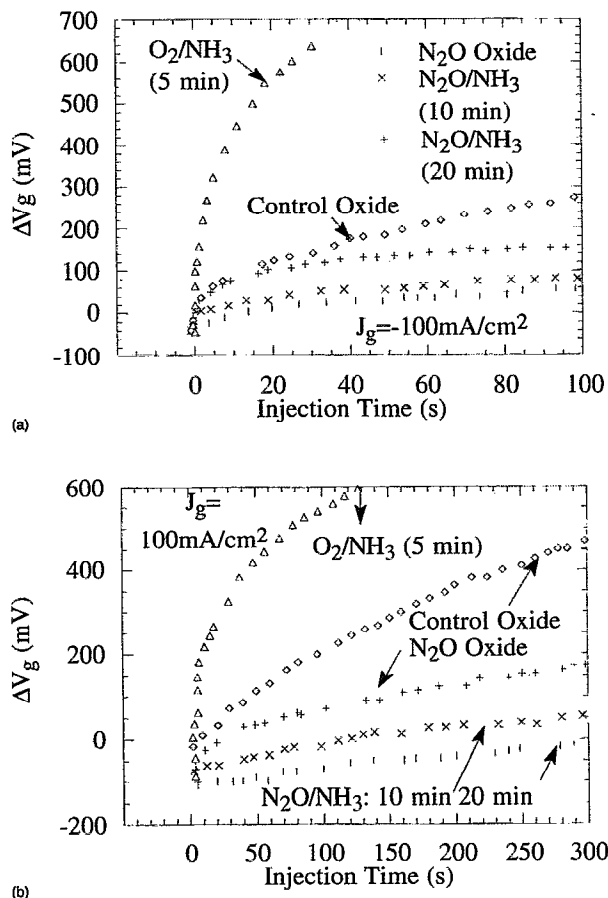


FIG. 4. Change in gate voltage required to maintain a constant current density of (a) -100 mA/cm^2 and (b) 100 mA/cm^2 in MOS capacitors with different gate dielectrics.

face property has been attributed to the growth of a strainless interface in the latter case. This may be another reason for the poor interface quality of NH_3 -nitrided SiO_2 annealed in N_2 .

Charge-trapping properties of NH_3 -nitrided N_2O grown oxides can also be explained with the knowledge of the chemical compositions. Charge trapping properties are studied by monitoring the change in gate voltage necessary to maintain a constant current through the oxide during gate or substrate injection. A positive ΔV_g indicates net electron trapping and a negative ΔV_g indicates net hole trapping. The slope of the ΔV_g versus stress-time plot gives an indication of trap generation and filling rate. Since our XPS analysis shows the presence of silamine groups throughout the entire bulk of NH_3 -nitrided N_2O oxide, one would expect to see a finite amount of electron trapping under constant current stress from gate injection in the bulk of the NH_3 -nitrided N_2O oxides, similar to what has been observed in NH_3 -nitrided SiO_2 , since hydrogen related species are a major source of electron traps. However, as seen from the results in Fig. 4(a), it is interesting to note that devices with NH_3 -nitrided N_2O oxide show even less electron trapping than control oxide and much less electron trapping than NH_3 -nitrided SiO_2 , even though NH_3 -nitrided N_2O and NH_3 -nitrided SiO_2 films have comparable density of silamine

groups. Study is underway to understand the mechanism for suppressed electron trapping in NH_3 -nitrided N_2O oxides. It is worth noticing that the field-assisted trap generation rate in all N_2O -based oxides is negligible. In addition, NH_3 -nitrided SiO_2 samples show the highest rate of field-assisted trap generation among all the samples.

Figure 4(b) shows the charge trapping in the oxide film as a consequence of substrate injection. Nonequilibrium condition due to deep depletion was avoided by shining light on the device. It is interesting to note that the net field-assisted trap generation rate in NH_3 -nitrided N_2O oxides is even lower than in N_2O oxides. In fact, an increase in NH_3 -nitridation time suppresses the trap generation rate even further. This phenomenon can be explained as follows. The presence of strong $\text{Si}-\text{N}$ bonds in place of strained $\text{Si}-\text{O}$ bonds makes trap generation less likely. Since NH_3 -nitrided samples have higher amounts of nitrogen and hence more $\text{Si}-\text{N}$ bonds (as also seen from XPS results), these samples are expected to have higher resistance to field-assisted trap generation and the degree of resistance should increase with the amount of nitrogen. The results in Fig. 4(b) are consistent with this hypothesis.

XPS analysis of NH_3 -nitrided N_2O films confirms that NH_3 nitridation increases the nitrogen concentration significantly, resulting in significant improvement in diffusion barrier properties of NH_3 -nitrided oxides as shown in a previous work by Yoon *et al.*³

In conclusion, we have studied the effects of NH_3 nitridation on the chemical and electrical properties of N_2O oxides, and their comparison with NH_3 -nitrided SiO_2 . Correlation between the chemical and electrical properties of NH_3 -nitrided oxides has been made to explain the superior quality of NH_3 -nitrided N_2O oxides with regard to immunity to interface state generation, charge trapping under electrical stress, and the enhanced diffusion barrier properties.

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