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Correlation between Chemical Structure and Electrical Properties of NH_3-Nitrided N_2O Oxides

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In this paper, effects of NH_3 nitridation on chemical and electrical properties of N_2O oxides and their correlation have been studied. Compared with NH_3-nitrided SiO_2, NH_3 nitridation does not degrade the electrical properties of N_2O oxides, resulting in superior impurity diffusion barrier properties while preserving excellent interface immunity to hot carrier injection and much lower charge trapping. The presence of N-O bond in N_2O based oxides is found to play a key role in determining the interface hardness of the dielectric.

INTRODUCTION

Oxynitrides have been found to be an attractive replacement for conventional SiO_2 as gate dielectric. The motivation for using oxynitrides is that the nitrogen incorporated at the oxide/silicon interface strengthens the interface and renders it immune to hot-carrier damages[1,2]. The other important reason for incorporating nitrogen is that it acts as a good barrier to boron penetration which comes about when p^+-polysilicon is used as the gate electrode in MOSFETs[3,4]. While NH_3 nitrided SiO_2 are known to have high amounts of nitrogen in the film (1-5 at. %), N_2O grown oxides have low levels of nitrogen[5,6]. Hence, in order to retain the excellent reduction in interface state generation and at the same time improve the barrier to boron penetration, one needs to increase the nitrogen levels in N_2O oxides. We have accomplished this by performing NH_3 nitridation of N_2O grown oxides[6]. The electrical data presented in Ref. 6 shows that the NH_3 nitridation of N_2O oxide does stop boron penetration effectively without degrading the interface reliability properties. In this paper we have used x-ray photoelectron spectroscopy (XPS) to study the chemical modification of N_2O oxide upon NH_3 nitridation and its correlation with electrical properties. A comparitive study of the bonding structures and electrical properties of NH_3-nitrided N_2O oxides and NH_3 nitrided SiO_2 shows that unlike NH_3-nitrided SiO_2, NH_3-nitrided N_2O 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 N-O bond in N_2O based oxides.

EXPERIMENT

Samples for angle-resolved XPS (ARXPS) study were prepared by rapid thermal processing (RTP). N_2O oxide was prepared by RTP at 950°C for 10 seconds in N_2O ambient and nitrided N_2O oxide samples were prepared by RTP of N_2O oxide at 950°C for 20 seconds in NH_3 ambient. The thickness of the XPS samples were measured by ellipsometry to be less than 25Å. MOS capacitors with n^+-polysilicon gate were used for electrical characterization and were fabricated on 3-5 Ω.cm (100) p-type Si substrate. N_2O and O_2 gate oxides were grown at 950°C by using conventional resistance heated furnace. Some of the N_2O oxides were NH_3 nitrided at 900°C for different duration (0-20 minutes). O_2 oxides were nitrided at 900°C for 5 minutes in NH_3 ambient. All oxides were annealed in N_2 at 950°C for 20 minutes. The thicknesses of the gate oxides were measured to be 80Å.

RESULTS & DISCUSSION

In order to identify the chemical bonding structure at the interface of the various dielectrics, deconvolution of N 1s spectra obtained from ARXPS was performed. Fig. 1 shows the deconvolution of N 1s spectra of N_2O oxide. Two peaks corresponding to Si≡N bond at 397.6 eV[7] and Si_2=N-O bond at 399.8 eV are observed. Due to the absence of hydrogen in the nitridation ambient, we do not see any evidence of hydrogen-related bonds in the XPS analysis. Deconvolution of N 1s spectra for NH_3-nitrided N_2O oxides shows a peak at a binding energy of 398.6 eV in addition to Si≡N peak and

Si_2=N-O peak throughout the bulk of the oxide (Fig. 2a-c). The peak at 398.6 eV has been identified by Bischoff *et al.* as the position of a silamine group ($Si-N=H_2$)[8]. 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.

Results shown in Fig. 3 indicate that varying NH_3 nitridation time from 0 to 20 minutes does not degrade ΔD_{it} after injection of $0.2C/cm^2$ of charge. In fact, all N_2O-based oxides show equally good resistance to stress induced interface state generation as compared to pure O_2 oxide and NH_3 nitrided O_2 oxide. This result is an indication of the fact that even though subsequent nitridation of N_2O in NH_3 ambient increases the intensity of Si≡N bond and adds hydrogen-based silamine bonds, it does not alter the chemical structure which is responsible for excellent immunity to interface state generation in N_2O oxides. These observations indicate that perhaps the N-O bond incorporated during N_2O oxidation plays a significant role in determining the interface hardness to hot-carrier injection. Additionally, no such N-O bond is observed in the XPS analysis of NH_3 nitrided O_2 oxide (not shown). The absence of the N-O bond in NH_3 nitrided O_2 oxides is probably the main reason for the lack of improvement in interface quality of O_2 oxides upon NH_3 nitridation. The relationship between the absence of N-O bonds and the poor interface quality of NH_3 nitrided O_2 oxide also provides evidence for the role of N-O bond in determining immunity to interface state generation. It is also important to bear in mind that the NH_3 nitrided SiO_2 sample used in our experiments is annealed in N_2 unlike NH_3 nitrided SiO_2 samples which are annealed in O_2 (popularly known as reoxidized nitrided oxides ROXNOX). 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 due to the growth of a strainless interface in the latter case[9]. This maybe 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/substrate injection. Our XPS analysis shows the presence of silamine groups throughout the entire thickness of NH_3 nitrided N_2O oxide. Hence we expect to see finite amount of electron trapping in the bulk of the NH_3 nitrided N_2O oxides since hydrogen related species are a major source of electron-traps[10]. As seen from Fig. 4, N_2O oxide shows very small electron trapping under gate injection due to the absence of hydrogen complexes as also seen from XPS data (Fig. 1), while NH_3 nitrided samples show some electron trapping. It is worth noticing that the field-assisted trap generation rate in all N_2O-based oxides is negligible. On the other hand, NH_3 nitrided SiO_2 samples show a high rate of field-assisted trap generation. This is due to the weakening of the interface caused by network deformation from light nitridation[11].

NH_3 nitridation of oxide films increases nitrogen concentration, as confirmed by XPS, and hence improves boron stopping properties. Diffusion barrier properties of NH_3 nitrided oxides and N_2O oxides have been illustrated in a previous work by Yoon *et al.*[6]. Our XPS analysis confirms the fact that NH_3 nitridation of oxides does increase the nitrogen content significantly.

CONCLUSIONS

We have demonstrated that there exists a strong correlation between the chemical/structural and electrical properties of NH_3 nitrided N_2O oxides. It has been shown that the quality of the dielectric with regard to immunity to interface weakening from hot-carrier injection and the enhanced diffusion barrier properties of NH_3 nitrided oxides can be explained with the knowledge of the bonding structure.

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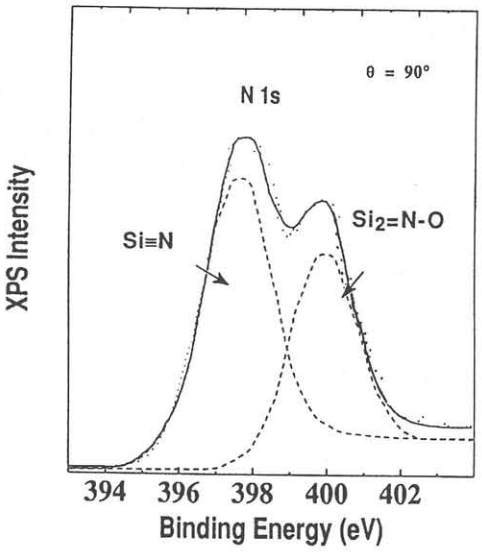

Fig. 1 Curve-fit of N 1s spectra obtained by ARXPS of N_2O Oxide at take-off angle of 90°.

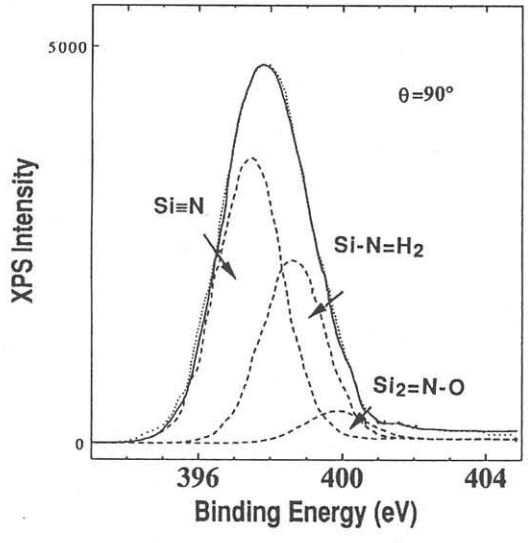

Fig. 2 (a) Curve-fit of N 1s spectra obtained by ARXPS of NH_3-nitrided N_2O Oxide at take-off angle of 90°.

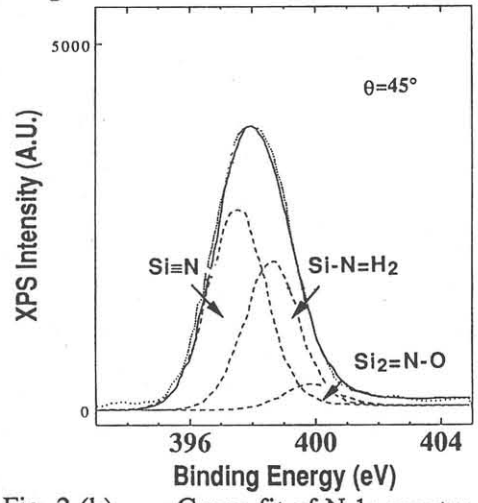

Fig. 2 (b) Curve-fit of N 1s spectra obtained by ARXPS of NH_3-nitrided N_2O Oxide at take-off angle of 45°.

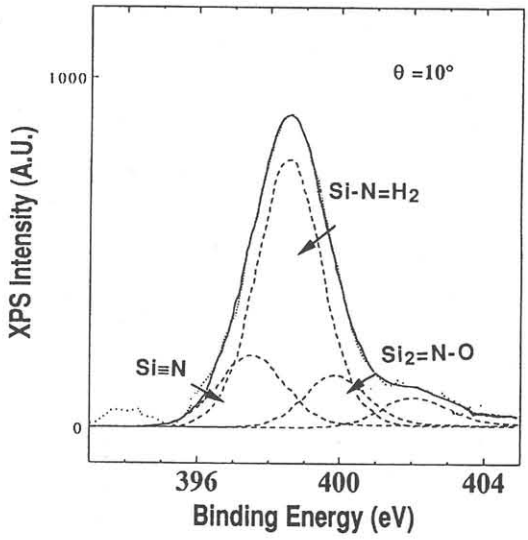

Fig. 2 (c) Curve-fit of N 1s spectra obtained by ARXPS of NH_3-nitrided N_2O Oxide at take-off angle of 10°.

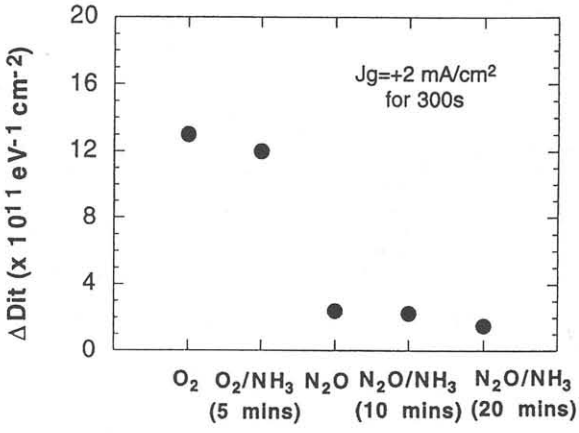

Fig. 3 ΔD_{it} for pure oxide, N_2O oxide, NH_3-nitrided N_2O-oxide after injection of $0.2C/cm^2$ of charge.

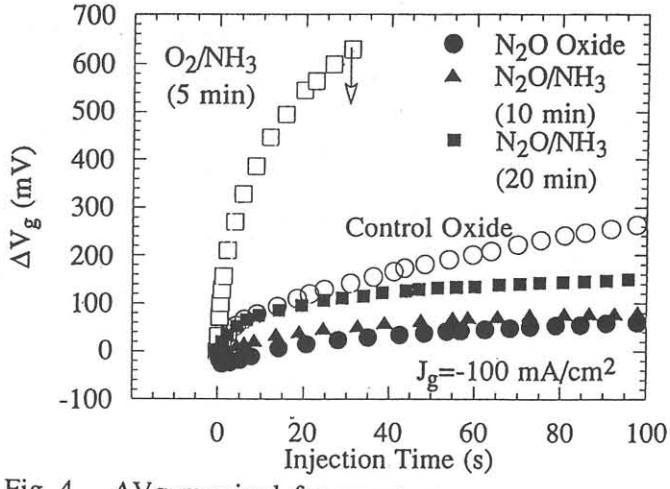

Fig. 4 ΔVg required for constant current stress experiment for gate-injection.