Effects of reoxidation on band alignment in N-incorporated SiON films as a function of sequential thermal annealing in NO and NH$_3$

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The effects of reoxidation on the band structure of N-incorporated SiON films were investigated as a function of thermal treatment in NO and NH$_3$. Reoxidation-associated changes in band gap and valence band offset of the N-incorporated SiON films prepared by sequential thermal annealing in both NO and NH$_3$ were less than those observed for the nitrided film prepared by thermal annealing in only NH$_3$. The differences in band-alignment characteristics of the nitrided films that resulted from use of different nitridation methods were strongly related to the depth distribution of N and the chemical states of N bonded to Si. © *2008 American Institute of Physics.*
[DOI: 10.1063/1.2955835]

The questionable reliability of ultrathin gate dielectrics is one of the most serious challenges to the scaling of ultralarge scale integration devices. Moreover, attempts to reduce the thickness of SiO$_2$ to less than 2 nm have clearly demonstrated that high gate leakage current and poor resistance to boron penetration are limitations associated with the use of SiO$_2$.[1]

N incorporation into SiO$_2$ films has advantages such as resistance to dopant diffusion and suppression of interfacial layer growth.[2] In general, N is incorporated into the SiO$_2$ films either via thermal processes that use gaseous NO, N$_2$O, and NH$_3$ or by plasma nitridation.[3,4] The challenges associated with thermal nitridation using gaseous NO, N$_2$O and NH$_3$ include adjustment of the N-profile and hydrogen-induced charge trapping.[5–7] Nitridation using NH$_3$ produces SiO$_2$ films with relatively high nitrogen concentrations compared to films that are nitrided using other gases. In these films, diffusion of nitrogen that is displaced by O during reoxidation to remove hydrogen is impaired. Thus, films that undergo nitridation with NH$_3$ produce SiON films that contain low concentrations of nitrogen.[8] In contrast, nitridation by thermal annealing in gaseous N$_2$O or NO is a more attractive method because these gases are hydrogen-free. SiON films prepared using NO preferentially incorporate nitrogen near the film interface compared to films prepared using other thermal nitridation processes at equivalent temperatures. Moreover, the electrical characteristics of films prepared via thermal nitridation with NO are superior, with reduced leakage currents and interface-defect densities.[6] In the present study, SiON films were fabricated by sequential thermal annealing, first in NO gas and then in NH$_3$ gas, for comparison of the sequential and single nitridation processes using gaseous NH$_3$ and NO. Next, the SiON films were post-annealed in ambient O$_2$ to remove the effects, such as charge trapping, of NH$_3$ on hydrogen and to observe the behavior of N incorporated into the films.

The focus of the present study was on changes in band alignment of N incorporated into SiO$_2$ films resulting from use of sequential thermal annealing treatment with NO and NH$_3$, and on reoxidation effects. The band alignment of SiON films was dependent on both the annealing method used for nitridation of the films and on the reoxidation process. That is, the band characteristics, as a function of sequential thermal annealing and reoxidation, were strongly related to the chemical states and depth distribution of the N that was incorporated into the films.

Thermal SiO$_2$ films with a thickness of 3 nm were grown on (100) orientated *p*-type Si wafers that had been cleaned chemically using the standard Radio Corporation of America method to remove organic and metallic residues. Nitrogen was incorporated either by rapid thermal annealing either in ambient NH$_3$ or NO, or by sequential thermal annealing in both gaseous NO and NH$_3$ at 720 °C. After thermal nitridation, reoxidation was performed by rapid thermal annealing in gaseous O$_2$ at 720 °C. Changes in band gap and valence band offset that resulted from sequential thermal annealing and reoxidation were investigated using reflection electron-energy-loss spectroscopy (REELS) and high-resolution x-ray photoelectron spectroscopy (HR-XPS), respectively. REELS is well suited to the determination of band gap in ultrathin oxide films because of the low electron energy.[9] The valence band offset and chemical-state analysis of SiON films were assessed by HR-XPS. To obtain elemental and quantitative information about depth direction, medium energy ion scattering (MEIS) analysis was carried out with a 100 keV proton beam in the double-alignment configuration, which reduces contributions from the crystalline Si substrates.[10]

Figure 1 shows REELS energy-loss spectra with a primary electron energy of 1000 eV. Band gap (E_g) values were determined from the point of intersection obtained by the linear fit line with maximal negative slope.[11] As shown in

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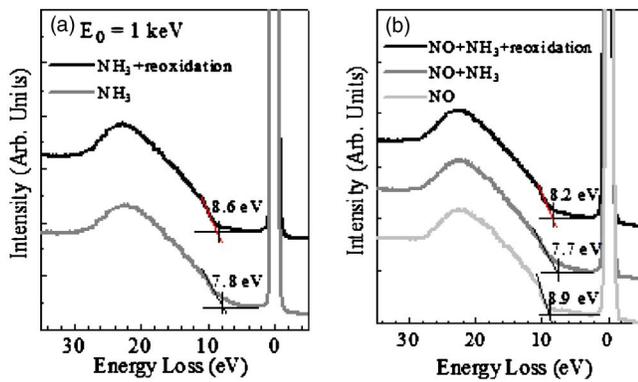
FIG. 1. (Color online) REELS spectra (a) for SiON films prepared by thermal annealing in NH_3 gas (b) for SiON films prepared by sequential thermal annealing in ambient NO and NH_3.

FIG. 2. Valence band spectra (a) for SiON films prepared by thermal annealing in NH_3 gas (b) for SiON films prepared by sequential thermal annealing in ambient NO and NH_3e.

Figs. 1(a) and 1(b), the band gaps of the SiON films prepared by thermal annealing in NH_3 (SiON-I) and by sequential thermal annealing in NO and NH_3 (SiON-II) were 7.8 ± 0.1 eV and 7.7 ± 0.1 eV, respectively. These band gap values were much less than that of the SiON annealed in ambient NO (8.9 ± 0.1 eV). The small change in band gap of the SiON film annealed in NO, in comparison with that of the SiO_2 film, can be attributed to the light concentration of N distributed at the interface between the film and the Si. The inelastic mean free path values for SiO_2 films, dependent on primary electron energy, were ~1.2, ~1.7, and ~2.9 nm at 300, 500, and 1000 eV, respectively.[12] In nitrided SiO_2 film, the mean free path was decreased because of the increased film density. Thus, at an energy value of 1000 eV, we could not measure the energy-loss spectra and band gap at the interfacial region of SiON/Si. After reoxidation, the band gap of SiON-II films increased to approximately 8.2 ± 0.1 eV, while the band gap of the SiON-I films increased to ~8.6 ± 0.1 eV. The difference in band gap values of nitrided SiON films was closely related to the electronic structure of the film, i.e, the changes in the N content of the film and defect states after thermal annealing treatment affect the electronic structure of SiO_2 films, which resulted in a reduction in the band gap.

Band structures of N-incorporated SiON films show that the highest valence band consists of N $2p$ states and O $2p$ states, and the lowest conduction band is dominated by the Si $3s$.[12] Because the N $2p$ state is at a higher energy level than the O $2p$ state, by approximately 1 eV, the band gap is reduced because of changes in the valence band. Thus, we investigated the valence band structure of SiON films in relation to the nitridation method employed using XPS, as shown in Fig. 2. The valence band maximum (VBM) of SiON films was determined from the point of intersection obtained by extrapolation, as shown in Fig. 2. The indexed values in Fig. 2 show the valence band offset (ΔE_v) between VBMs of the Si and SiON films. The valence band offset values show that the SiON-II film is less than that of SiON-I film (~4.2 eV versecs. ~4.6 eV). After reoxidation, the valence band offset increased to ~4.9 eV in the SiON-I film and to ~4.4 eV in the SiON-II film. The electronic structure near the valence band was dominated by the N $2p$ states that formed as a result of N incorporation. When the film is nitrided using NH_3 gas, the increase in valence band values can also be affected by the hydrogen effect—as thermally activated and outdiffused hydrogen allows nitrogen to be re-
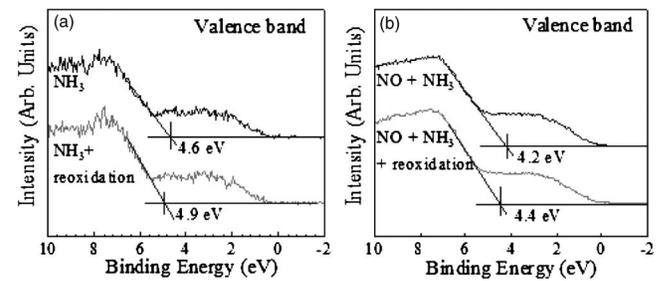
placed by oxygen more effectively during the reoxidation process.[7] That is, N $2p$ states were reduced and valence bands were increased, as shown Fig 2(a). Consequently, a change in valence band values affects the band gap variation. Electron barrier heights (conduction band offset, ΔE_c) were calculated from the band gap and valence band offset using the following equation: $\Delta E_c = E_g(\text{oxide}) - E_g(\text{Si}) - \Delta E_v$ (oxide/Si).[13] Band alignments, as a function of the nitridation method and of reoxidation, are summarized in Table I.

After reoxidation, the change in N content in the depth profile can be dependent on the nitridation process because the bonding state of N is affected by the nitridation process and the oxidation process acts as an exchange process of N with O.[4] Thus, in order to clarify the effect of the N content after reoxidation, detailed elemental composition and depth distribution were analyzed using MEIS, as shown in Fig. 3. The nitrogen concentration of the film prepared by thermal annealing in NO was mostly incorporated at the interface (average concentration incorporated into the film was low: ~2.3 at %), as shown in Figs 3(b) and 3(d), which is consistent with reported data.[1] For the SiON-I and SiON-II films, the nitrogen-peak areas show that the nitrogen incorporated in the film decreased gradually with increasing film depth. Also, the average nitrogen concentrations of the two films were similar, ~6.24 and ~6.84 at. %, respectively. However, after reoxidation, the SiON-I film had a lower nitrogen-peak height (~3.98 at. %) than that of the SiON-II film (~6.75 at. %). As shown in Fig. 3(b), the width of the oxygen peak increased after reoxidation of the SiON-II film, which is indicative of an increase in film thickness: the peak broadens, while the total amount of the N content is maintained after reoxidation. Figures 3(c) and 3(d) show the calculated depth profile data. In these results, both SiON-I and SiON-II films have a similar distribution of N. In the case of the SiON-I films, the thickness of the film did not increase after reoxidation, which was a result of the decrease in N concentration with thermally activated hydrogen.[1] On the other hand, and of greater interest, is that most of the nitrogen concentration of the SiON-II films remained uniform

TABLE I. Summary of band gap and band offsets values for SiON films as a function of thermal annealing method.

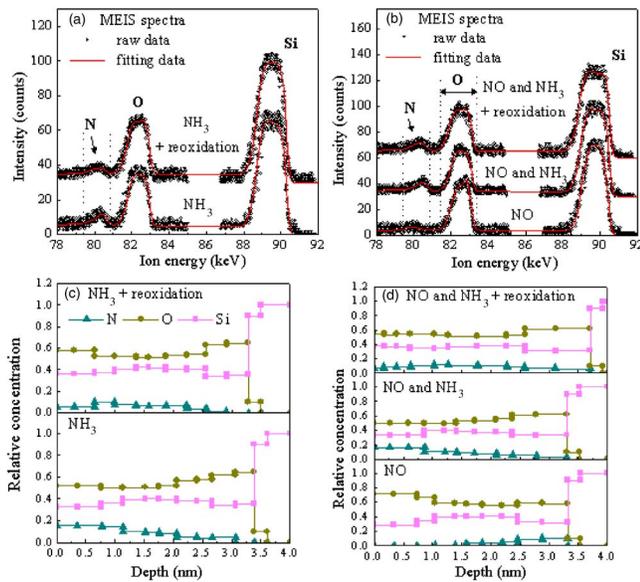|	NH_3	NH_3 + reoxidation	NO and NH_3	NO and NH_3 + reoxidation
E_g (Ev)	7.8 ± 0.1	8.6 ± 0.1	7.7 ± 0.1	8.2 ± 0.1
ΔE_C (eV)	2.1 ± 0.1	2.5 ± 0.1	2.4 ± 0.1	2.7 ± 0.1
ΔE_v (eV)	4.6 ± 0.1	4.9 ± 0.1	4.2 ± 0.1	4.4 ± 0.1

FIG. 3. (Color online) MEIS energy spectra (a) for SiON films prepared by thermal annealing in NH$_3$ gas (b) for SiON films prepared by sequential thermal annealing in ambient NO and NH$_3$, and depth profiles fitted by simulation (c) for SiON films prepared by thermal annealing in NH$_3$ gas (d) for SiON films prepared by sequential thermal annealing in ambient NO and NH$_3$. In addition, respective changes in energy spectra and depth profiles after reoxidation are shown.

from the surface to the interface region, compared to that of the SiON-I films after reoxidation. In particular, nitrogen remained at the interface between the film and the bulk, which can contribute to a low band gap and valence band value at the interface.

To investigate changes in chemical states associated with band structure, XPS analysis was performed. Figure 4 shows N 1*s* spectra for SiON films as a function of the nitridation method and of reoxidation. N 1*s* spectra were deconvoluted into N1, N2, and N3, located at 397.9, 398.7, and 399.5 eV, respectively.[11] Each component represents N1$-$Si$_3$N$_4$, N2-[Si$_3$O]$_x$N, and N3-Si$_2$ON considering the nearest N, sec-
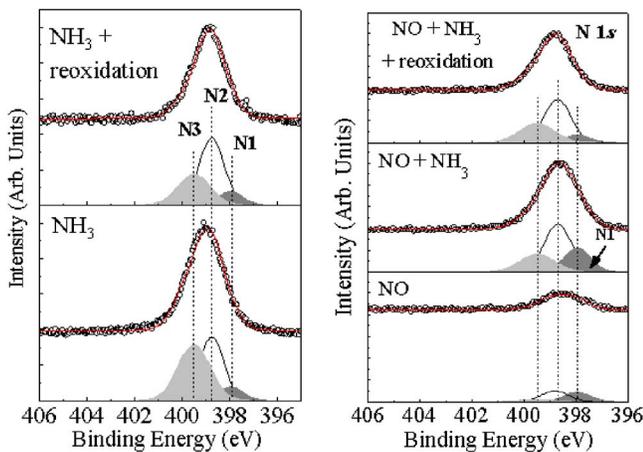

FIG. 4. (Color online) XPS spectra of N 1*s* for SiON films as a function of sequential thermal annealing and reoxidation.

ond nearest N, and neighbors of N based on previously reported theoretical values.[11] The SiON-II films had a high N1 chemical state relative to that of the SiON-I films. In contrast, SiON-I films had a high N3 chemical state relative to that of the SiON-II films. Based on these results, it was concluded that the nitridation method affects the N chemical state, similar to the differences in N depth distribution observed in the MEIS analysis. After reoxidation, the N3 chemical state of SiON-I films and the N1 chemical state of SiON-II films were significantly decreased. Changes in the chemical states of N as a function of sequential thermal annealing and reoxidation can be explained by corresponding changes in band structure. In SiON films, the N1 chemical state dramatically altered both the band gap and valence band offset, based on the results obtained from the SiON-II films. However, the N3 chemical state had a greater effect on band gap than on valence band offset, as observed for the SiON-I films. Thus, these results indicate that the difference in N configuration between N1 and N3 bonded to Si, is a significant difference, which alters the band structure.

In summary, the effects of reoxidation on band alignment in N-incorporated SiON films were investigated as a function of sequential thermal treatment in ambient NO and NH$_3$. The difference in the reduction in band gap was related to the chemical state of the Si–N bonding. After reoxidation, the band gap and valence band of the N-incorporated SiON films was significantly affected by the addition of NO during the annealing process, as compared to films prepared by thermal annealing using only NH$_3$.

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