

Nitridation for HfO₂ high-*k* films on Si by an NH₃ annealing treatment

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The characteristics of nitrated HfO₂ films suggest that the diffusion of Si from the Si substrate to the film surface is induced by annealing in an NH₃ ambient and that the incorporation of N is closely related to the diffusion of Si. Changes in the core-level energy state of the N 1s peaks of nitrated HfO₂ films indicate that the quantity of N incorporated into the film drastically increases with increasing annealing temperature, especially at temperatures over 900 °C. The incorporated N is mostly bonded to Si that diffused from the Si substrate into the film, while some N is incorporated to HfO₂ at high annealing temperature. Some molecular N₂ is generated in the film, which is easily diffused out after additional annealing. Moreover, the chemisorbed N in the film is not completely stable, compared to that at the interfacial region: i.e., the N in the film predominantly out diffuses from the film after additional annealing in a N₂ ambient. © 2006 American Institute of Physics. [DOI: 10.1063/1.2202390]

Fundamental studies of the incorporation of nitrogen into high-*k* dielectrics have been limited to a few oxides. In particular, the physical characteristics associated with the nitridation of HfO₂-based high-*k* gate dielectrics have been investigated recently, since nitridation can, in practice, improve scalability, lower leakage, and higher breakdown fields. Quevedo-Lopez *et al.* observed that the penetration of B atoms from polycrystalline Si through Hf silicate films can be effectively reduced by the incorporation of N.¹ Kang *et al.* reported that a HfO_xN_y gate dielectric, prepared by reactive sputtering, showed a lower equivalent oxide thickness and a lower leakage current density.² Recently, an interesting finding reported that bulk Hf–N bonds in reactive-sputtered HfO_xN_y are not stable during postdeposition annealing.³ However, the cause of the thermal instability of nitrated HfO_xN_y films has not been examined. Moreover, the role of N at the interfacial layer, which critically affects the electrical characteristics, has not been clarified. Thus, the nature of the electronic structure of nitrated films is very important, in terms of understanding the behavior of N as a function of the thermal treatment.

In this study, we focused on the characteristics of N incorporated HfO₂ films grown on Si using an atomic layer deposition (ALD) system. The change in chemical state related to N incorporation for a postannealing treatment in an NH₃ atmosphere was investigated using medium energy ion scattering (MEIS), high resolution x-ray photoelectron spectroscopy (HRXPS), and near edge x-ray absorption fine structure (NEXAFS) analysis. HRXPS and NEXAFS spectra suggest that the incorporated N is bonded to the SiO₂ interfacial layer and the silicate film, but not to pure HfO₂. A variety of gas phases, including N₂ and NO_x, is observed

after the NH₃ annealing treatment at a point over a specific substrate temperature. During the NH₃ annealing treatment, the diffusion of Si from the substrate into the HfO₂ film is enhanced, resulting in a drastic increase in the interfacial layer and a change in the stoichiometry of the film. After annealing a sample in an NH₃ ambient, followed by a second annealing in inert gas of N₂, the amount of N and molecular N₂ incorporated into the film is drastically decreased, compared to that in the interfacial layer.

HRXPS and NEXAFS measurements were carried out at the Pohang accelerator laboratory on beamline 8A1, which is connected to an undulator, using a third generation synchrotron radiation source. The binding energy was calibrated with reference to the position of bulk Si 2p_{3/2} levels at $E_b = 99.2$ eV for the energy of each photon. The energy of the incident photons was fixed at 600 eV, thus providing a high photoionization cross section of Si 2p, Hf 4f, N 1s, and O 1s. A *p*-type Si (100) substrate with a resistivity of 2–5 Ω cm was cleaned using the Radio Corporation of America (RCA) method and the surface oxide was removed by treatment with a dilute HF solution. In order to stabilize and reduce the interfacial state, an ~10 Å layer of SiO₂ was included by a rapid thermal oxidation (RTO) process.⁴ The metal oxides were grown using an ALD system, which has a vertical warm wall reactor with a showerhead and a heated susceptor. HfO₂ films were grown at temperatures below 300 °C using HfCl₄ as a precursor and the film thickness was controlled at 15 Å for HRXPS and at 30 Å for NEXAFS and MEIS measurements. H₂O vapor served as the oxygen source and N₂ was supplied as the purge and carrier gas. The HfO₂ samples were subsequently annealed from 700 to 900 °C for 60 s in an NH₃ atmosphere.

Figure 1 shows MEIS spectra of HfO₂ films, prepared using different nitridation temperatures. It is clear that the Si

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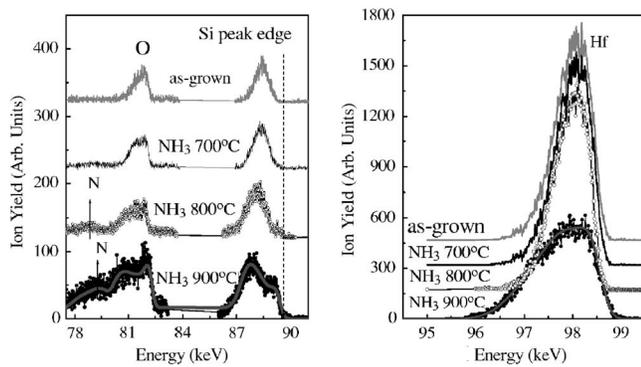


FIG. 1. MEIS spectra of as-grown and annealed HfO_2 films at temperatures of 700, 800, and 900 °C for 60 s. in an NH_3 atmosphere. The solid line in the spectrum of the sample annealed at 900 °C is the fitting data of the raw spectrum of the sample.

shoulder at a higher scattering energy than that caused by the Si substrate is present at the Si peak edge of 89.2 keV for annealing temperatures over 800 °C. Considering the elastic ion scattering using 100 keV H^+ ions, the peak edge at the higher energy region is caused by Si in the film or the Si substrate.⁷ Thus, the changes can be explained by agglomeration of HfO_2 film or diffusion of Si from the substrate to the film. In the case of agglomeration of HfO_2 film, HfO_2 intergranular voids would look like SiON at the top surface of the film. In ion scattering using MEIS, some incident ions that are scattered on the SiON surface would undergo a scattering process through HfO_2 agglomerates, while others would not. The scattering process should change the Hf peak; background and shoulder increase at the energy range less than 97 keV. However, no background and shoulder are observed, reflecting that the peak change in Si is caused by Si in the film, no Si substrate. The height of the Si shoulder is increased with increasing annealing temperature, indicating that, if the change is caused by diffusion of Si, the diffusion of Si from the Si substrate to the film is increased and high quantity of Si is incorporated into the HfO_2 film at a high annealing temperature of 900 °C. Thus, the change in the intensity and shape of Hf and Si peaks shows that diffusion starts at an annealing temperature of about 800 °C and drastically increases at temperatures over 900 °C. The incorporation of Si decreases the area of Hf for an as-grown HfO_2 film up to half and increases the film thickness by almost twice after an annealing treatment at 900 °C. Si diffusion is related to the interaction between HfO_2 and Si to form the Hf silicate layer.⁵

Another important finding is that the N concentration in the depth direction of the film changes with annealing temperature. The incorporation of N into the film is not effective at temperatures below 700 °C: i.e., the measured quantity of N is just below a few at. %. Peak positions for N in MEIS spectra also show that at an annealing temperature of 800 °C, the quantity of N incorporated into the film is perceptibly increased up to ~10 at. % and is almost concentrated at the interfacial region, while at 900 °C the N is significantly incorporated into the film up to ~26 at. % and is rather focused on film, not on interface. The changes in the N depth profiling data precisely coincide with the change in the Si depth profile that diffuses into the film. Thus, these results suggest that the incorporation of N can be enhanced in a HfO_2 film containing Si, but not in pure HfO_2 , which is very consistent with the findings reported in our previous

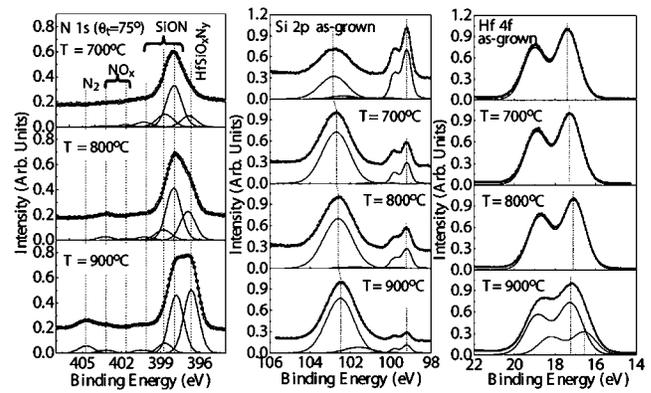


FIG. 2. XPS spectra of N 1s, Si 2p, and Hf 4f for 15 Å thick HfO_2 films at annealing temperatures from 700 to 900 °C in an NH_3 atmosphere.

study, i.e., that N is effectively incorporated into a $\text{HfO}_2\text{-Al}_2\text{O}_3$ alloy film rather than pure HfO_2 .⁴

In order to characterize the chemical bonding related to N, XPS spectra for N 1s, Si 2p, and Hf 4f were collected, as shown in Fig. 2. The change in N peak as a function of annealing temperatures shows the relationship of N with the complex oxide of the $\text{HfO}_2\text{-SiO}_2$ system more clearly. The raw spectra for different nitridation temperatures show clear variations in the line shape as well as peak maxima, suggesting that there are significant differences in the nitrogen depth profile and the chemical states. Through a more detailed and quantitative analysis, a curve fitting analysis disclosed that there are two nontrivial N components: i.e., 396.8 ± 0.1 eV (N1) and 397.8 ± 0.2 eV (N2). Minor high binding features can also be seen over 401 eV, which are caused by molecular N_2 and gaseous NO_x .⁶ N1 and N2 states are increased with increasing the annealing temperature. The most drastic change is the peak height of two major N1 and N2 peaks with nitridation temperature, which is consistent with the change in MEIS depth profile for the quantity of N as a function of temperature. Based on reported XPS results for SiON, the energy of N2 can be attributed to N species with three Si nearest neighbors ($\text{N} \equiv \text{Si}_3$).^{7,8} On the other hand, the corresponding N1 peak at 396.8 eV is not related to the chemical bond of Si–O–N compounds because the binding energy is higher than that for $\text{N} \equiv \text{Si}_3$. Changes in Si 2p and Hf 4f peaks as a function of annealing temperature provide an interpretation of the chemical bonding state. The gradual shift in the Si 2p peak to lower binding energy supports the view that the incorporated N is gradually increased, consistent with the change in the N1 peak because Si peak related to N bond is located at the lower binding energy position than that to O bond. A change in the shift of Hf peak is not clear up to an annealing temperature of 800 °C, while more distinct change occurred at 900 °C: i.e., the peak is broadened and it can be deconvoluted to two peaks. The lower binding energy state at 16.4 eV can be related to the Hf–O–N bond because the bonding energy of Hf–N (15.3–15.8 eV) can be shifted to higher binding energy state by incorporation of O into Hf–N bond.^{3,9} Based on the depth profiling data of MEIS spectra, the peak change of N 1s in XPS spectra indicates that the N1 and N2 are closely caused by nitridation of film and interface, respectively.

Changes in the molecular structure of HfO_2 as a function of annealing temperature were examined using NEXAFS. NEXAFS spectra of the O K edge and the N K edge in a

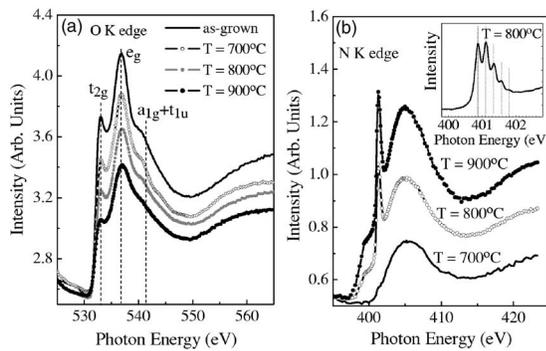


FIG. 3. NEXAFS spectra of (a) O K edge features of as-grown and annealed HfO_2 films at temperatures from 700 to 900 °C for 60 s in an NH_3 atmosphere. (b) NEXAFS spectra of the N K edge corresponding to the annealed HfO_2 films. The inset is the high resolution spectrum of the sharp peak that appeared at the annealing temperature over 800 °C.

HfO_2 film were collected and the results are shown in Fig. 3. In HfO_2 , the Hf metal d states are strongly hybridized with oxygen $2p$ orbitals, resulting in three peaks caused by unoccupied hybridized orbitals, t_{2g} (Hf $5d + \text{O } 2p\pi$), e_g (Hf $5d + \text{O } 2p\sigma$), and $(a_{1g} + t_{1u})$ (Hf $6s, 6p + \text{O } 2p$), in an octahedral symmetry.¹⁰ The peak positions of the O K edge features of HfO_2 , E_{d1} (for t_{2g}) = 533 eV, E_{d2} (for e_g) = 536.8 eV, and E_{SP} (for $a_{1g} + t_{1u}$) = 542 eV, are in good agreement with the reported data for HfO_2 .¹¹ The intensity ratio of the first two peaks shows that the Hf e_g orbitals are significantly strongly overlapped with oxygen p_z orbitals resulting in a much higher intensity than the reported data because the interface of the thin HfO_2 film (30 Å) distorts the octahedral symmetry.¹² No significant change in the O K edge spectrum was observed up to an annealing temperature at 700 °C. On the other hand, at an annealing temperature of over 800 °C, the intensity related to t_{2g} and $a_{1g} + t_{1u}$ is decreased and the full width at half maximum (FWHM) of the peaks is increased, which is caused by the incorporation of Si and N as shown in the MEIS spectra because the incorporation increases the dispersion of the Hf d band. The N K edge spectra also revealed the chemical state of N in HfO_2 film. Clearly two different states of N are present in the film as evidenced by a sharp and a broad peak. The broad feature at a higher energy position is related to excitation to the (Hf $6sp + \text{N } 2p$) states.¹¹ Moreover, the peak is caused by the excitation of the (Si $3sp + \text{N } 2p$) because the N interacts with the Si in the film and at the interface as shown in the XPS data. Another interesting finding is that the sharp absorption peak at 401 eV cannot be attributed to chemisorbed nitrogen because it is much too narrow. High resolution data show that the sharp peak is composed of five peaks, consistent with the peak caused by the molecular N_2 state, as shown in the inset of Fig. 2.

Finally, we investigated the characteristics of N depth profiling and chemical state, followed by an additional annealing treatment at 700 °C in a N_2 ambient after a nitridation treatment in an NH_3 atmosphere. The MEIS data show that the quantity of N is decreased after the additional annealing treatment, as shown in Fig. 4(a). In particular, the N content of the film is significantly decreased, while the quantity of N in the interfacial region is not in relative terms. The XPS data also support this conclusion, as shown in Fig. 4(b):

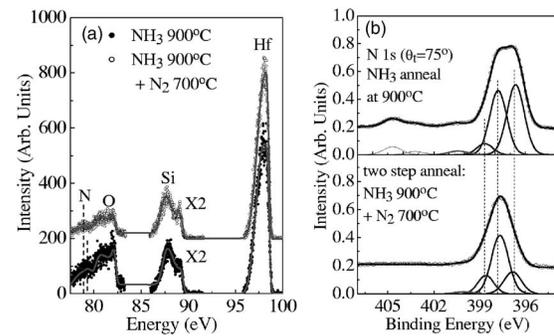


FIG. 4. Changes in (a) MEIS and (b) XPS spectra with additional annealing in N_2 ambient at 700 °C after the nitridation annealing at 900 °C using NH_3 . The solid lines in the MEIS data are the fitting results of the raw spectra.

i.e., N incorporated in the film is clearly decreased after the annealing treatment. In addition, various gas phases including molecular N_2 state disappear, which is reasonable because the states in the gas phase can easily out diffuse through the film during the additional annealing. Based on these results, we conclude that the incorporation of N in the film is not stably maintained, while N in the interfacial region is relatively stable.

In summary, the chemical state of N incorporated HfO_2 films was investigated and the physical properties were investigated. N was gradually added in the interfacial region at temperatures below 800 °C, while it was significantly incorporated into the film at a temperature of 900 °C, accompanied by the diffusion of Si from the substrate to the film. Moreover, the N incorporated into the film is relatively more unstable than that in the interfacial region when the NH_3 gas is used in the nitridation process.

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