Characteristics of HfO$_2$–Al$_2$O$_3$ laminate films containing incorporated N as a function of stack structure and annealing temperature

M.-H. Cho[a)]
Nano Surface Group, Korea Research Institute of Standards and Science, Daejon 305-600, Korea

K. B. Chung and C. N. Whang
Institute of Physics and Applied Physics (IPAP), Yonsei University, Seoul 120-749, Korea

D.-H. Ko
Department of Material Science and Engineering, Yonsei University, Seoul 120-749, Korea

H. S. Kim
Department of Material Science and Engineering, Seongkyunkwan University, Suwon 440-746, Korea

The properties of Al$_2$O$_3$–HfO$_2$ laminated films with incorporated N were investigated as a function of stack structure and annealing temperature by high-resolution x-ray photoelectron spectroscopy, and medium energy ion scattering (MEIS). The MEIS results indicate that the diffusion of Si from the Si substrate into film increased in the case where a film with a buffer layer of Al$_2$O$_3$ was present during the annealing at temperatures up to 800 °C, while it led to a relative suppression in a film with a HfO$_2$ buffer layer. The incorporation of N was gradually increased in the film with a buffer layer of Al$_2$O$_3$ on Si with annealing temperature, while the increase was abrupt in the film with a buffer layer of HfO$_2$ on Si at an annealing temperature of 900 °C. The N incorporated into the film was very unstable, resulting in out diffusion from the film after an additional annealing treatment. © *2005 American Institute of Physics.* [DOI: 10.1063/1.2147718]

High-k gate dielectrics such as HfO$_2$, ZrO$_2$, and rare-earth oxides have been studied as possible alternative gate dielectrics for future ULSI technology to replace conventional SiO$_2$ because of the decreased leakage current and improved reliability.[1–4] Among the high-k materials, HfO$_2$ is considered to be one of the most promising gate dielectrics for advanced complementary metal-oxide-silicon applications. HfO$_2$ is compatible with polysilicon, poly-SiGe, and TaN gates, and maintains a low equivalent oxide thickness to suppress the penetration of oxygen and impurities, although HfO$_2$ has not been shown sufficient thermal stability.[5–7] In order to improve thermal stability, an alloy of Hf-oxide containing Al-oxide or a HfO$_2$–Al$_2$O$_3$ laminate structure is applied to gate dielectrics.[8] In particular, the physical characteristics associated with the nitridation of HfO$_2$-based high-k gate dielectrics have recently been investigated, because nitridation improves scalability, leakage current, and breakdown fields.[9] Our previous study showed that, in a typical HfAlO alloy film, the majority of the N atoms are bonded to Al$_2$O$_3$, and not to HfO$_2$.[12] However, its thermal stability and the N depth profiling characteristics, which critically affect electrical characteristics, have not been clarified. Moreover, the electronic structure in nitrided alloy films, which has an effect on thermal stability, has not been considered yet, although a complete understanding of the behavior of N as a function of thermal treatment is important.

In this letter, we focus on the characteristics of N-incorporated HfO$_2$–Al$_2$O$_3$ laminate 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 atmosphere of NH$_3$ as a function of stack structure and whether the Si is in contact with the HfO$_2$ or Al$_2$O$_3$, was investigated using medium energy ion scattering (MEIS), near-edge x-ray absorption fine structure (NEXAFS), and high resolution x-ray photoelectron spectroscopy (HRXPS).

The MEIS spectra showed that the degradation of the laminate structure occurs gradually in the stack structure of an Al$_2$O$_3$ first-deposited film as the annealing temperature increases, but is abrupt in the stack structure of a HfO$_2$ first-deposited film at annealing temperatures of over 900 °C. During the NH$_3$ annealing treatment, the diffusion of Si from the substrate into the laminate film is enhanced, resulting in a drastic increase in the interfacial layer and the destruction of the stack structure. Moreover, the depth profile of N is not uniform, which is highly correlated with the depth profile for Si in the film. When the N in the film is highly concentrated and a buffer layer of an HfO$_2$ film is present, the system is relatively unstable and most of the N in the film out diffuses, compared to the film with a buffer layer Al$_2$O$_3$ film.

NEXAFS measurements were carried out at the Pohang accelerator laboratory on beamline 8A1 using a third-generation synchrotron radiation source. The XPS spectra were measured using monochromatic Al $K\alpha$ (1486.6 eV) with a PHI 5700 spectrometer The binding energy was calibrated with a reference to the position of bulk Si $2p_{3/2}$ levels at E_b=99.2 eV for the energy of each photon. MEIS measurements using a 100 keV H$^+$ beam was achieved in an incident beam along with Si (111) and blocking dip conditions, in order to extract only film information without a contribution from the substrate. A p-type Si (100) substrate with a resistivity of 2–5 Ω cm was cleaned using the 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 SiO$_2$ was included by a rapid thermal oxidation (RTO) process.[5] The metal oxides were grown using an ALD system, which has a vertical warm wall reactor with a showerhead and a heated susceptor.
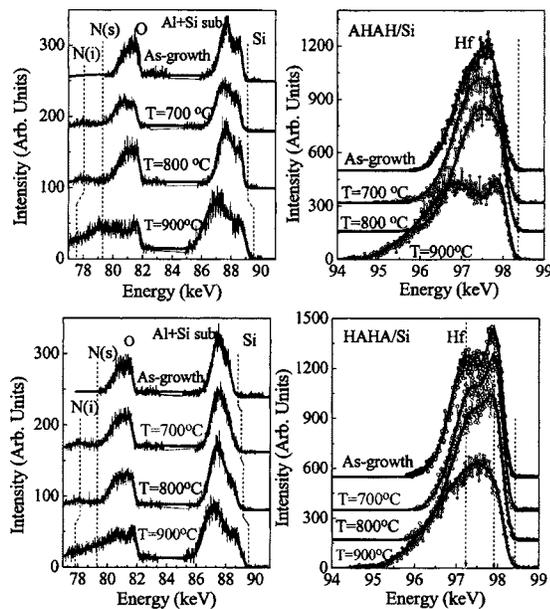
[a)]Electronic mail: mhcho@kriss.re.kr

87, 262906-1

FIG. 1. MEIS spectra of 4-nm-thick HfO_2-Al_2O_3 laminate films annealed at various temperatures from 700 to 900 °C in a NH_3 ambient. AHAH/Si and HAHA/Si represent the structure of Al_2O_3(1 nm)/HfO_2(1 nm)/HfO_2(1 nm)/Al_2O_3(1 nm)/HfO_2(1 nm)/ Al_2O_3(1 nm)/SiAl$_2$O$_3$(1 nm)/HfO_2(1 nm)/Si and , respectively.

Al_2O_3 and HfO_2 films were each grown at temperatures below 300 °C using $Al(CH_3)_3$ and $HfCl_4$ as a precursors. H_2O vapor served as the oxygen source and N_2 was supplied as the purge and carrier gas. Laminate structures with the composition HfO_2(10 Å)/Al_2O_3(10 Å)/HfO_2(10 Å)/Al_2O_3(10 Å)/Si (HAHA) and Al_2O_3(10 Å)/ HfO_2(10 Å)/Al_2O_3(10 Å)/HfO_2(10 Å)/Si (AHAH) were fabricated. The films were annealed using a rapid thermal process (RTP) in an ambient of NH_3 from 700 to 900 °C for 2 min.

The change in laminate structure and the concentration of N in depth profiles with nitridation temperature was investigated by means of MEIS. Figure 1 shows the MEIS spectra of an HfO_2−Al_2O_3 laminate film prepared at different nitridation temperatures. The clear finding is that the leading edge of the peak near the scattering energy of 89 keV is shifted to higher scattering energy with increasing annealing temperature, indicating that Si atoms have diffused into the laminate film. In this case, the diffusion behavior of the Si atom is dependent on the stack structure; i.e., the diffusion process in a film with a buffer layer of Al_2O_3 proceeds gradually, while it is suppressed at temperatures up to 800 °C and becomes more drastic at 900 °C in the film with a buffer layer of HfO_2. Moreover, the MEIS spectra of the Hf peaks indicate a change in laminate structure with increasing annealing temperature; i.e., the laminate structure is gradually disrupted in the film with a buffer layer of Al_2O_3, while the stably maintained structure is abruptly disturbed at an annealing temperature of 900 °C in a film with a buffer layer of HfO_2. The correlation of structural change with the diffusion of Si indicates that the diffusion process is associated with structural destruction. Another interesting finding is that the content of N in the depth direction is dependent on the stack structure of the laminate film as well as structural changes. Nitrogen that is incorporated below an annealing temperature of 800 °C is largely located in the interfacial region of the both stack structures as denoted by N(i) in the
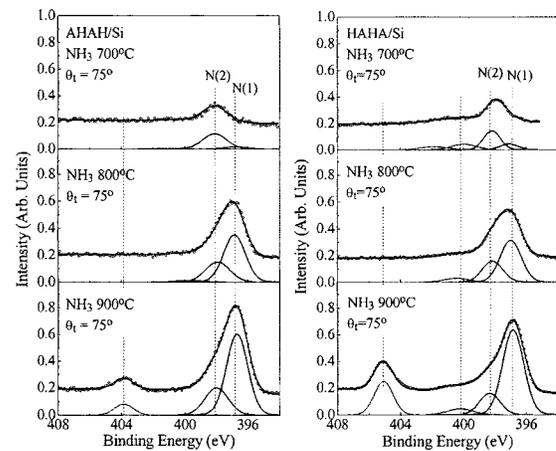

FIG. 2. XPS spectra of N 1s in AHAH/Si (left side) and HAHA/Si (right side) films after annealing at various temperatures from 700 to 900 °C in a NH_3 ambient.

spectra. However, at an annealing temperature of 900 °C in which the N content is extensively incorporated, the N is largely distributed in the film, and not locally concentrated at the interface, as evidenced by the N peak position at the interface and the surface. Moreover, the quantity of N incorporated into the film with a buffer layer of HfO_2($\sim$42 at. %) is higher than that in the film with a buffer layer of Al_2O_3($\sim$23 at. %) when the film is annealed at a temperature of 900 °C. This discrepancy in the quantity of N between the two stack structures indicates that another extrinsic factor has a critical effect on the incorporation process. The differences in the MEIS spectra depending on the stack structure provide the reason for this. The height and width of the shoulder of the Si peak, which is related to the amount of Si that diffuses into the film with a buffer layer of HfO_2 is higher and wider than that for a film with a buffer layer of Al_2O_3 when the films are annealed at 900 °C. This indicates that the quantity of Si atom that diffuses from the substrate into the film with a buffer layer of HfO_2 is greater than that of the film with a buffer layer of Al_2O_3. In addition, the characteristic shape of the Hf and N spectra indicate that the N profile in the depth direction is not uniform and dependant on the Si profile in the film.

In order to characterize the chemical bonding related to N and its thermal stability, XPS and NEXAFS spectra were collected, as shown in Figs. 2 and 3. The change in the N peak as a function of stack structure shows the relationship between N and the diffused Si content more clearly. The raw spectra at different nitridation temperatures show clear variations in line shape as well as peak maxima, suggesting that there are significant differences in the nitrogen depth profile and chemical states. Through a more detailed and quantitative analysis, a curve fitting analysis disclosed that there are two nontrivial N components: 396.8 ± 0.2 eV (N1), 398 ± 0.2 eV (N2). A minor high binding feature is also found at over 404 eV, which is caused by N_2.[10] The change of intensity in the N1 and N2 peaks shows very different tendency; i.e., the peak height of N1 is drastically increased as the annealing temperature increases, especially after an annealing temperature of 900 °C, while that of N2 is not significantly changed with annealing temperature. The drastic change in peak height with nitridation temperature, which is consistent with the change in MEIS depth profile for the
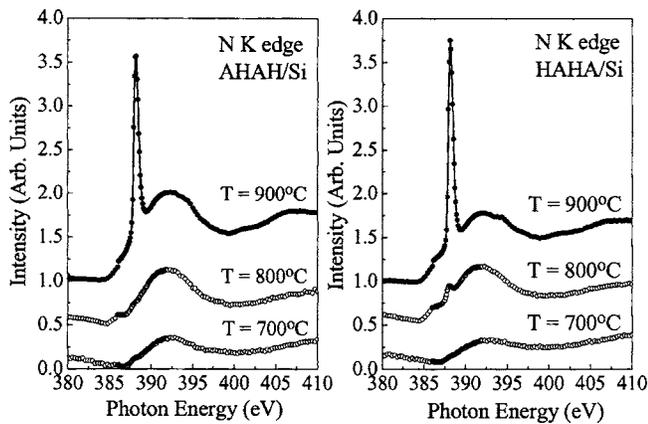
FIG. 3. NEXAFS spectra of the N K edge in AHAH/Si (left side) and HAHA/Si (right side) films after various annealing temperatures from 700 to 900 °C in a NH_3 ambient. The sharp peak is caused by molecular N_2 and the broad peaks are related to chemically N bonded with the film.

FIG. 4. MEIS spectra of 4-nm-thick HfO_2-Al_2O_3 laminate films after additional annealing at a temperature of 700 °C in a N_2 ambient (T_2). The peak caused by N is drastically decreased after T_2 in both the AHAH/Si and HAHA/Si films. The insets are N $1s$ XPS spectra of the laminate films after the additional annealing treatment (T_2).

quantity of N and Si with the annealing temperature, indicates that the binding states of N1 and N2 are closely related to Si in the film and the interface, respectively. Based on reported XPS results for SiON and HfON, the energy of N1 at 396.8 eV can be attributed to N species related with Si, Hf, and Al in the film, while the corresponding N2 peak at 398 eV results from the chemical bond of Si–O–N compounds at the interface.[11] The NEXAFS spectra also support the formation of N_2 at 900 °C.[12] The change in the broad peak related to chemically bonded N in the film and a sharp peak corresponding to N_2 correspond precisely with the change in the XPS peak. N_2, in the molecule state, is observed only at annealing temperatures over 900 °C, which suggests that the some of dissociated high density of NH_3 gas at the high temperature contributes to the incorporation of N into the film and another portion is converted into molecular N_2 because of its stable molecule structure. The quantity of chemically bonded N and molecular N_2 show an opposite tendency; at 900 °C, the quantity of molecular N_2 in the film with a buffer layer of Al_2O_3 is greater than that in the film with a buffer layer of HfO_2, while the quantity of chemically bonded N in the HfO_2 first-deposited film is greater than that in an Al_2O_3 first-deposited film. This indicates that the formation of molecular N_2 is dependent on thermodynamical factors; i.e., when the N is readily reacted with a film, the formation of a molecular N_2 state is relatively suppressed. From N depth information on the laminate films as a function of nitridation temperature as shown in the MEIS data, the N1 and N2 peaks to a N peak in the film and at the interface, respectively, because a large quantity of N at a nitridation temperature of 900 °C is drastically incorporated into the film, while its concentration at the interface remains unchanged.

Finally, we investigated the characteristics of N depth profiling after an additional annealing treatment at 700 °C in a N_2 ambient, as shown in Figs. 4(a) and 4(b). The MEIS data shows that the quantity of N is drastically decreased after the additional annealing treatment. In particular, the MEIS peak, corresponding to remnant N, showed that the small quantity of N (below 5 at. %) is uniformly distributed in both regions at the interface and the film. In comparing the pure HfO_2 film with a laminate structure containing an Al_2O_3 layer, which reacts more readily with N, more N remains in the laminate film, both in the film and the interfacial
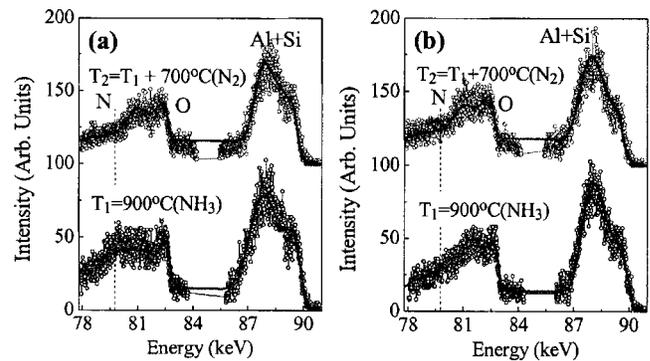
region.[12] Another interesting finding is that the highly incorporated N in the stack structure of the film with a buffer layer of HfO_2 is more unstable than that of a film with a buffer layer of Al_2O_3; i.e., more N in the film with a buffer layer of HfO_2 diffuses out than in the film with a buffer layer of Al_2O_3. Consequently, the quantity of N remaining in the film with a buffer layer of HfO_2 after an additional annealing treatment is only slightly higher than that in the film with a buffer layer of Al_2O_3.

In summary, structural changes and depth profiles of incorporated N as a function of nitridation temperature in an NH_3 ambient were investigated. The chemical state of the incorporated N and its thermal stability was also assessed. The quantity of incorporated N and its depth profile is dependant on the stack structure of the laminate films. The diffusion of Si from the Si substrate as a function of stack structure has a significant influence on the structural changes and N incorporation. However, most of the incorporated N is not stably maintained in the film after sequential annealing in a N_2 ambient.

[1] M. L. Green, E. P. Gusev, R. Degraeve, and E. L. Garfunkel, J. Appl. Phys. **90**, 2057 (2001).
[2] K. Krisch, M. L. Green, F. H. Baumann, D. Brasen, L. C. Feldmann, and L. Manchanda, IEEE Trans. Electron Devices **43**, 982 (1996).
[3] C. M. Perkins, B. B. Triplett, P. C. McIntyre, K. C. Saraswat, S. Haukka, and M. Tuominen, Appl. Phys. Lett. **78**, 2357 (2001).
[4] G. Scarel, E. Bonera, C. Wiemer, G. Tallarida, S. Spiga, M. Fanciulli, I. L. Fedushkin, H. Schumann, Y. Lebedinskii, and A. Zenkevich, Appl. Phys. Lett. **85**, 630 (2004).
[5] M.-H. Cho, Y. S. Roh, C. N. Whang, K. Jeong, D.-H. Ko, S. W. Nahm, J. H. Lee, N. I. Lee, and K. Fujihara, Appl. Phys. Lett. **81**, 472 (2002).
[6] S. K. Kang, S. Nam, B. G. Min, S. W. Nam, D.-H. Ko, and M.-H. Cho, Appl. Phys. Lett. **83**, 2004 (2003).
[7] V. V. Afanasev, A. Stesmans, L. Pantisano, and T. Schram, Appl. Phys. Lett. **86**, 232902 (2005).
[8] M. Y. Ho *et al.*, Appl. Phys. Lett. **81**, 4218 (2002).
[9] M.-H. Cho *et al.*, Appl. Phys. Lett. **84**, 5243 (2004).
[10] O. Björncholm, A. Nilsson, A. Sandell, B. Hernnas, and N. Martensson, Phys. Rev. Lett. **68**, 1892 (1992).
[11] C. S. Kang, H.-J. Cho, K. O. Onishi, R. Nieh, R. Choi, S. Gopalan, S. Krishnan, J. H. Han, and Jack C. Lee, Appl. Phys. Lett. **81**, 2593 (2002).
[12] R. Feifel, M. Andersson, G. Öhrwall, S. L. Sorensen, M. N. Piancastelli, M. Tchaplyguine, O. Björneholm, L. Karlsson, and S. Svensson, Chem. Phys. Lett. **383**, 229 (2004).