Change in phase separation and electronic structure of nitrided Hf-silicate films as a function of composition and post-nitridation anneal

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

K. B. Chung
Institute of Physics and Applied Physics, Yonsei University, Seoul 120-749, Korea

D.-H. Ko
Department of Ceramics Engineering, Yonsei University, Seoul 120-749, Korea

The thermal stability and electronic structure of nitrided $x\text{HfO}_2 \cdot (100-x)\text{SiO}_2$ (HfSiO) ($x=25\%$, 50%, and 75%), prepared using an NH_3 annealing treatment, were investigated. The quantity of N incorporated into the Hf-silicate film was dependent on the mole fraction of SiO_2 in the film: i.e., a silicate film containing a high mole fraction of SiO_2 contained a higher quantity of N, resulting in the suppression of phase separation. In particular, the incorporated N easily diffuses out through a silicate film that contains a small quantity of SiO_2 during the post-nitridation anneal, while in a film with a high quantity of SiO_2, it is relatively stable. The phase separation effect in the nitrided film with a low SiO_2 mole fraction was significantly influenced by the stability of N in the film and interface. © *2006 American Institute of Physics*. [DOI: 10.1063/1.2355478]

High dielectric constant (k) films, such as alloys of ZrO_2, HfO_2, and their silicates, have received a great deal of attention because of their potential use as alternative gate dielectrics for replacing conventional SiO_2 or oxynitride because excessive leakage current and gate dielectric reliability can be effectively improved using high-k films.[1] In particular, hafnium silicates ($HfSi_xO_y$) have been shown to be compatible with various gate materials because of their good thermal stability, when in contact with the gate.[2] However, the thermal stability of a film and interfacial interactions are closely related to the composition of the Hf-silicate layer: interfacial interactions between the Hf-silicate film and the Si substrate are enhanced in films containing a high quantity of SiO_2, resulting in the suppression of phase separation.[3,4]

The incorporation of nitrogen has been extensively studied in gate dielectric films including SiO_2 and various high-k films since they play a key role in present and near future metal-oxide-semiconductor devices.[5] Reports have recently appeared regarding incorporating nitrogen into high-k metal oxides such as HfO_2 and ZrO_2 to improve the thermal stability of high-k gate dielectrics because the incorporated N can overcome the insufficient immunity of the dielectrics, thus improving the diffusion barrier during the subsequent thermal process.[6,7] In particular, since N incorporation significantly improves the thermal stability of Hf-silicate films, $HfSiO_xN_y$ is one of the most desirable materials for use in next-generation device applications. Toyoda *et al.* supplemented the chemical bonding state in N incorporated HfSiO films and achieved a good stability of N.[8] However, the thermal stability of the incorporated N as a function of composition has not been considered in detail, although it can critically affect the reliability of the gate dielectric and the threshold voltage in a device.

In this study, we focused on the electronic structure and interfacial reactions of nitrided HfSiO films on Si using an annealing treatment in an NH_3 ambient. We investigated the change in chemical state related to the thermal stability of N incorporated into $x\text{HfO}_2(100-x)\text{SiO}_2$ as a function of film composition and post nitridation annealing using x-ray photoelectron spectroscopy (XPS) and near edge x-ray absorption fine structure (NEXAFS). The stoichiometry in the depth direction was also assessed by medium energy ion scattering (MEIS) using a H^+ beam with an incident energy of 101 keV.

A p-type Si substrate with a resistivity of $2-5\ \Omega$ cm was cleaned using the RCA method. Metal oxides were grown using an atomic layer deposition (ALD) system, which has a vertical warm wall reactor with a showerhead and a heated susceptor. SiO_2 and HfO_2 films were each grown at temperatures below 280 °C using tris(dimethylamido)silane and tetrakis(ethylmethylamido) hafnium, respectively, as precursors. H_2O vapor served as the oxygen source and N_2 was supplied as the purge and carrier gas. The SiO_2 incorporated Hf–Si–O were grown by the alternate ALD process, with the number of cycles for HfO_2 and SiO_2 repeated to mix the SiO_2 content in a controlled manner. $(HfO_2)_x(SiO_2)_{1-x}$ films 4 nm thick on Si with three different compositions, 25 mol % HfO_2-75 mol % SiO_2 ($x=0.25$), 50 mol % HfO_2-50 mol % SiO_2 ($x=0.5$), and 75 mol % HfO_2-25 mol % SiO_2 ($x=0.75$), respectively, were deposited by ALD. The films were nitrided in an NH_3 ambient at 900 °C and additionally annealed in a N_2 ambient at 800 °C for 1 min as a post-nitridation anneal (PNA) using rapid thermal anneal.

Figure 1 shows N $1s$ core level XPS spectra for 4 nm thick Hf-silicate films containing various HfO_2 fractions. The clear finding is that the quantity of N decreases with increasing HfO_2 fraction, suggesting that the incorporated N is preferentially bonded to Si, not Hf in the silicate films. Moreover, after PNA, the change in the amount of N in the film is dependent on the fraction of HfO_2, indicating that the incorporated N is relatively unstable in the film with a high frac-
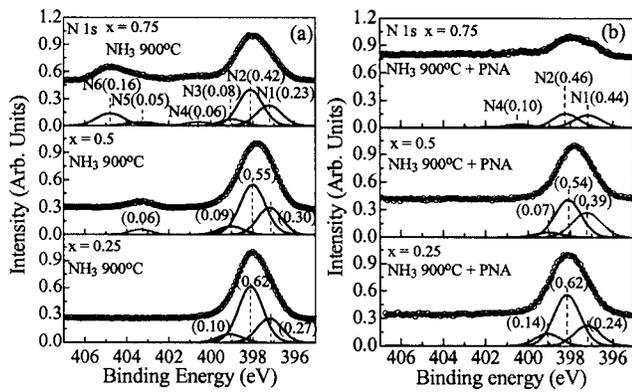

[a)]Electronic mail: mhcho@kriss.re.kr

FIG. 1. XPS peak spectra of N 1 s according to HfO$_2$ mole fractions (x =0.25, 0.5, 0.75) for as-grown Hf-silicate films. The right side shows a sample annealed in an NH$_3$ ambient at 900 °C and the left side shows an additionally annealed sample as a PNA in a N$_2$ ambient at 800 °C. The at. % of the incorporated N content in the samples annealed at 900 °C in an NH$_3$ ambient at 900 °C are ~14, ~19, and ~20 for x=0.75, 0.5, and 0.25, respectively. The detailed portion of the N contents is represented in parentheses.

FIG. 2. XPS peak spectra of Hf 4f according to HfO$_2$ mole fractions: (left side) x=0.75 and (right side) x=0.25. The peak of the as-grown film is compared with those of the nitrided and PNA samples. The nitridation temperature is 900 °C in an NH$_3$ ambient and an additional anneal temperature as a PNA is 800 °C in a N$_2$ ambient.

tion of HfO$_2$. A recent study reported that a higher N concentration using plasma nitridation yields more Si≡N bonds and they are very stably retained in the SiO$_2$ film after PNA,[9] corresponding to our result, showing that the N incorporated into the film with high SiO$_2$ fraction is very stable. Therefore, based on the reported results, some of the N that are bonded with Si are chemically stable in the film even after PNA, while N combined with HfO$_2$ is not firmly maintained. In order to clarify the chemical state of N in the film, the N 1s XPS spectra are deconvoluted. In all samples investigated, three main peaks in several N 1s peaks were observed for the peak positioned at ~397.2 eV (N1), 398.1 eV (N2), and 404.7 eV (N6). From the N binding energy, the main peak at ~397.2 eV can be attributed to N atoms to which three Si atoms are each bonded in a planar structure, N≡Si.[9] Although the cause for the case of N1 and N2 is not clear, it can be related to N species with three nearest Si neighbors from the reported results.[10] The N2 species is different from N1 only with respect to the second-nearest neighbors: i.e., N2 corresponds to nitrogen atoms that are dispersed within the SiO$_2$ matrix, while N1 corresponds to those incorporated into Si interfacial layers. The minor peaks for N3 and N4 can be attributed to nonstoichiometric silicon oxynitride and O$_2$ =N–Si formation, because the binding energy of the N 1s peak for SiN$_x$ species shifts their binding energy to a much higher level, depending on the x and nitrogen atoms that are bound to oxygen atoms.[11] The chemical states positioned at very high binding energy at 403.2 eV (N5) and 404.7 eV (N6), which can be assigned to molecular N$_2$ gas, are also observed in the Hf-silicate film during the nitridation process. The existence of two different chemical states caused by molecular N$_2$ gas can be explained by an extra-atomic relaxation effect, since the atomic relaxation effect can differently affect the N$_2$ molecule according to its surroundings.[12] The molecular state is not generated in the film with a high SiO$_2$ fraction, while the unstable N$_2$ gas in the film with a high HfO$_2$ fraction diffuses out after PNA.

Figure 2 indicates that the thermal stability is significantly dependent on the stability of N in the film. The clear conclusion is that no change occurs in the film with a high SiO$_2$ fraction after PNA, while distinct changes in the peak
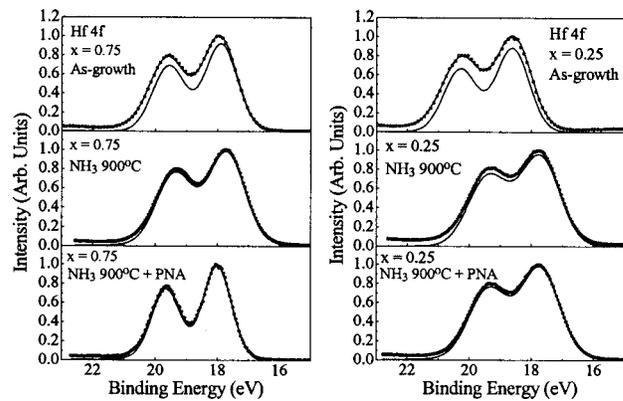
shape and position are detected in the film with a low SiO$_2$ fraction. The peak shift to a higher binding energy can be explained by the decrease in the quantity of N after PNA, considering the role of N in the film as a modifier of ionic bonding characteristics. Moreover, the most interesting finding is that the broad Hf 4f peak of the film with a low SiO$_2$ fraction is changed into a sharp characteristic Hf 4f peak. Since the broad Hf 4f peak in the silicate film is caused by a dispersion effect as a result of intermixing between HfO$_2$ and SiO$_2$, the change indicates that phase separation is not completely suppressed in the film with a high HfO$_2$ fraction after PNA.

The NEXAFS spectra of the O K edge clearly show the change in the molecular structure of Hf–Si–O, as shown in Fig. 3. The O K-edge spectra of HfO$_2$ are directly related to the oxygen p-projected density of the states, which consists of four unoccupied hybridized orbitals, t_{2g} (Hf 5d+O 2$_p\pi$), e_g (Hf 5d+O 2$_p\sigma$, a_{1g} (Hf 6s+O 2$_p$), and t_{1u} (Hf 6$_p$+O 2$_p$), assuming an octahedral symmetry. N incorporation suppresses phase separation in Hf-silicate films with a high HfO$_2$ mole fraction even when a high nitridation temperature of 900 °C is used, as shown in the spectra without any characteristic peak caused by the unoccupied hybridized orbitals of HfO$_2$. However, phase separation is not completely disturbed by the incorporation of N into a film with a high HfO$_2$
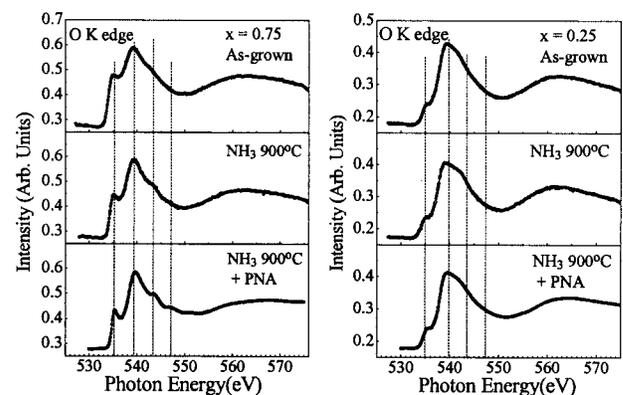

FIG. 3. Change in NEXAFS spectra of the O K edge in Hf-silicate films with a high HfO$_2$ mole fraction (x=0.75) and a low HfO$_2$ mole fraction (x=0.25). The peak of the as-grown film is compared with those of the nitrided and PNA samples.
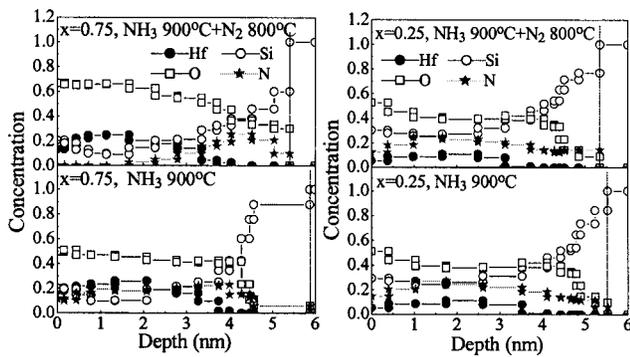
FIG. 4. The quantities of Hf, Si, O, and N contents from the MEIS spectra are calculated and their fraction represented with different HfO_2 mole fractions.

mole fraction; the most distinct change is observed in the appearance of the peaks caused by a_{1g}, t_{1u}, and t_{2g}. The appearance of the peaks clearly shows that HfO_2 is extracted from the mixture of SiO_2 and HfO_2 in a film with a high mole fraction of HfO_2 ($x=0.75$) during PNA. On the other hand, no change in the spectrum of the film with a low mole fraction of HfO_2 ($x=0.25$) during the nitridation process is obvious, even after PNA.

Phase separation phenomena and interfacial reactions were investigated using MEIS spectra to observe stoichiometric changes in the depth direction, providing a high depth resolution of $0.3–0.5$ nm, as shown in Fig. 4. When the nitrided film was additionally annealed at 800 °C in a N_2 ambient as a PNA, the most interesting change in the peak was related to N. The areal density of N incorporated in the film with $x=0.25$ is about 25% higher than that in the film with a high HfO_2 fraction. The N contained in both the film and interface is not significantly changed in the case of the film with a low HfO_2 fraction, while that in the film with a high HfO_2 fraction had almost diffused out. The remaining N in the film with a high HfO_2 fraction is located only at the interface, as shown in the indicated area of the MEIS spectra. The noticeable change in N quantity in the depth direction indicates that the formation of stable Si≡N bonds in Hf-silicate film with a high SiO_2 fraction can be related to the thermal stability of the film, resulting in the effective suppression of the phase separation. However, unstable N bonds in Hf silicate with a high HfO_2 fraction easily diffuse out, resulting in the separation of the film with HfO_2 and SiO_2 after PNA, as shown in the spectra of Hf $4f$ in XPS and O K edge in NEXAFS. A previous study showed that phase separation is dependent on two factors, the fraction of HfO_2 and the interfacial diffusion of Si from the substrate.[3] In this case, the change in the quantity of SiO_2 in the depth direction is induced by such factors and results in phase separation.

However, no change in the Si and Hf peak of MEIS spectra was observed, indicating that the intrusion of SiO_2 grains into HfO_2 matrix layer or the extraction of SiO_2 at the film surface does not occur during PNA. Since the nitrided layer at the interfacial Si region blocks the diffusion of Si, interfacial interactions have no effect on phase separation. The expected shape in the depth direction of the phase separated film through fitting the raw spectra and the above information is that very small grains such as nanosized SiO_2 with an amorphous structure are uniformly distributed into the HfO_2 matrix with a polycrystalline structure.

In summary, the chemical state of nitrided Hf–Si–oxide films as a function of the mole fraction of HfO_2 and PNA was investigated from the point of view of a change in phase. Peak changes for Hf and N in XPS indicate that the stability of N incorporated into the Hf-silicate film is closely related to phase separation. The N in the film with a high HfO_2 fraction is not stably maintained after PNA, resulting in phase separation of HfO_2 and SiO_2 in the film. The interfacial nitrided layer is very stable even after PNA, which affects the phase separation effect in the depth direction. The stably maintained N in the film effectively suppresses the effects of phase separation, while that in the interfacial layer completely hinders the phase separation.

[1] G. D. Wilk, R. M. Wallace, and J. M. Anthony, J. Appl. Phys. **89**, 5243 (2001).

[2] M. R. Visokay, J. J. Chambers, A. L. P. Rotondaro, A. Shanware, and L. Colombo, Appl. Phys. Lett. **80**, 3183 (2002).

[3] M.-H. Cho, K. B. Chung, C. N. Whang, D. W. Lee, and D.-H. Ko, Appl. Phys. Lett. **87**, 242906 (2005).

[4] S. Stemmer, Y. Li, B. Foran, P. S. Lysaght, S. K. Streiffer, P. Fuoss, and S. Seifert, Appl. Phys. Lett. **83**, 3141 (2003).

[5] M. L. Green, E. P. Gusev, R. Degraeve, and E. L. Garfunkel, J. Appl. Phys. **90**, 2057 (2001).

[6] C. S. Kang, H.-J. Cho, K. Onishi, R. Nieh, R. Choi, S. Gopalan, S. Krishnan, J. H. Han, and J. C. Lee, Appl. Phys. Lett. **81**, 2593 (2002).

[7] C. Hinkel and G. Lucovsky, Appl. Surf. Sci. **216**, 124 (2003).

[8] S. Toyoda, J. Okabayashi, H. Takahashi, M. Oshima, D.-I. Lee, S. Sun, S. Sun, P. A. Pianetta, T. Ando, and S. Fukuda, Appl. Phys. Lett. **87**, 182908 (2005).

[9] F. N. Cubaynes, V. C. Venezia, C. Van der Marel, J. H. M. Snijders, J. L. Everaert, X. Shi, A. Rothschild, and M. Schaekers, Appl. Phys. Lett. **86**, 172903 (2005).

[10] J. W. Kim, H. W. Yeom, K. J. Kong, B. D. Yu, D. Y. Ahn, Y. D. Chung, C. N. Whang, H. Yi, Y. H. Ha, and D. W. Moon, Phys. Rev. Lett. **90**, 106101 (2003).

[11] H. Kobayashi, T. Mizokuro, Y. Nakato, K. Yoneda, and Y. Todokoro, Appl. Phys. Lett. **71**, 1978 (1997).

[12] O. Björneholm, A. Nilsson, A. Sandell, B. Hernnäs, and N. Mrtensson, Phys. Rev. Lett. **68**, 1892 (1992).