

Electronic structure and thermal stability of nitrated Hf silicate films using a direct N plasma

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The thermal stability and electronic structure of nitrated $x\text{HfO}_2(100-x)\text{SiO}_2$ (HfSiO) ($x=30\%$, 55% , and 70%), prepared using a direct N plasma treatment, were investigated. N 1s spectra of nitrated Hf silicate films indicate that complex chemical states are generated. In particular, energy states with a high binding energy are stable, even after a postnitridation annealing. The quantity of N incorporated into the film is not dependent on the mole fraction of HfO_2 in the film, while the thermal stability of the N in the film is significantly influenced by the fraction of HfO_2 present. The thermal stability of the N in the film critically affects the composition and thickness of the film: i.e., after the postnitridation annealing, the thickness of the silicate film and the quantity of Hf and N are decreased, as the result of the dissociation of unstable Hf–N bonds. © 2006 American Institute of Physics. [DOI: 10.1063/1.2374852]

Hf silicate thin films have emerged as an attractive material among high dielectric films because of their compatibility with various gate materials owing to their good thermal stability when in contact with the gate.¹ Moreover, Hf silicate has an improved crystallization temperature and superior thermal stability, when in contact with a Si substrate and a poly-Si gate electrode.² Although the crystallization temperature of silicate is improved as the result of the incorporation of amorphous SiO_2 into the HfO_2 , the Hf silicate alloy can readily separate into two SiO_2 and HfO_2 phases due to the large local gradient in SiO_2 chemical potential and local stress at the interface.³ In order to improve the thermal stability of high- k gate dielectrics, the incorporation of nitrogen into high- k metal oxides is a powerful technique, because the incorporated N can overcome the insufficient resistance to the crystallization and phase separation.⁴ Our previous study showed that the phase separation and the quantity of N in the Hf silicate film is critically dependent on the mole fraction of SiO_2 in the film.⁵ Although the results of the nitridation of Hf silicate films suggest that the thermal stability of N in the film can be related to the quantity of SiO_2 present, the change in electronic structure and stoichiometric change in the depth direction, which is closely related to the thermal stability of a nitrated silicate film, has not been investigated systematically.

In this study, we focused on the electronic structure and thermal stability of nitrated HfSiO films on Si using a direct nitrogen plasma treatment. We investigated the change in chemical state related to the thermal stability of $x\text{HfO}_2(100-x)\text{SiO}_2$ with N incorporated as a function of film composition and postnitridation annealing (PNA) using x-ray photoelectron spectroscopy (XPS) and near edge x-ray absorption fine structure (NEXAFS). The composition in the depth direction was also assessed by medium energy ion scattering (MEIS).

The findings indicate that the chemical states of N incorporated into the Hf silicate film and the thermal stability of these states are clearly dependent on the mole fraction of

SiO_2 . N, when incorporated into a silicate film, is present in various chemical states. In particular, some of the bonding states of N in the film are related to HfO_2 , resulting in a very unstable chemical state. A greater quantity of unstable N bonding related to HfO_2 and N_2 gas in the molecular state is generated in a Hf silicate film with a higher mole fraction of HfO_2 . After the PNA treatment, the molecular N_2 disappears and the unstable chemical states decrease. The most important finding is that the film thickness shrinks and the stoichiometry of the film, especially the quantity of Hf and N, changes after the postnitridation annealing treatment.

A p -type Si substrate with a resistivity of 2–5 Ω cm was cleaned using the RCA method. Metal oxides were grown using an atomic layer deposition (ALD) system. 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. 3-nm-thick $(\text{HfO}_2)_x(\text{SiO}_2)_{1-x}$ films were grown on Si, by ALD, with three different compositions, 30 mol % HfO_2 –70 mol % SiO_2 ($x=0.30$), 55 mol % HfO_2 –45 mol % SiO_2 ($x=0.55$), and 70 mol % HfO_2 –30 mol % SiO_2 ($x=0.70$). The films were directly nitrated in a nitrogen plasma at room temperature and then further annealed in a N_2 ambient at 700 °C for 5 min using a rapid thermal annealing.

In order to characterize the chemical bonding related to N, XPS spectra for N 1s, Si 2p, and Hf 4f were collected after the plasma nitridation. The raw spectra of N 1s for samples with different HfO_2 fractions show clear variations in the broad peak shape as well as peak maxima, as shown in Fig. 1. Through a more detailed and quantitative analysis, a curve fitting analysis disclosed that numerous nontrivial N components are present, suggesting that significant differences exist in the chemical states in nitrated Hf silicate films prepared using NH_3 gas and a N plasma. For the case of a thermally nitrated Hf silicate film using NH_3 , our previous report showed that the nitrated chemical state is detected to have three main peaks, which is relatively simple, compared to the plasma nitrated chemical state.⁵ However, in compar-

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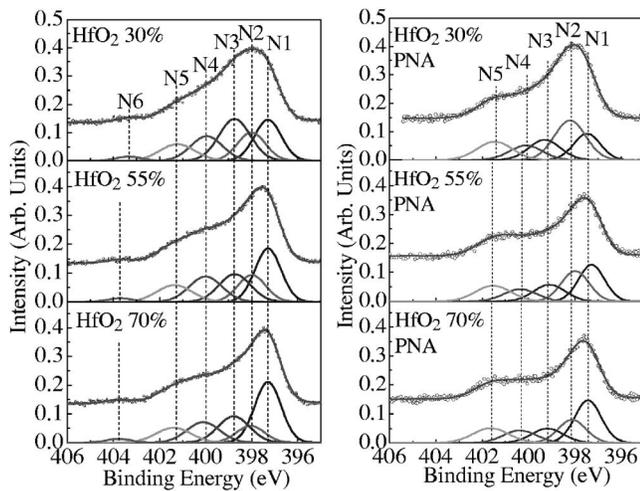


FIG. 1. XPS peak spectra of N 1s as a function of HfO₂ mole fraction ($x = 0.3, 0.5,$ and 0.7). The left side shows spectra of N 1s in as-grown samples and the right side shows spectra of samples after PNA in N₂ ambient at 700 °C.

ing the change in the N peak shape as a function of the HfO₂ fraction and the PNA treatment, the nitrated peak in Fig. 1 is more convoluted and complex and can be assigned to six peaks. From an inspection of the raw spectra of a nitrated sample, it appears that there are at least three major nitrogen species present, as evidenced by N 1s components at 397.3, 398.7, 401.2 eV, denoted as N1, N3, and N5, respectively. Other binding features can also be obtained from the curve fitting analysis through an investigation of changes in peak shape of the nitride sample with a HfO₂ fraction and a PNA 398.0 eV (N2), 400.0 eV (N4), and 403.3 eV (N6). Peaks, corresponding to N1 and the other major component N2, are unambiguously related to N species with three Si nearest neighbors (N≡Si₃).⁶ The N2 species is different from N1 only in the second nearest neighbors, in which the oxygen atom constituent Si [N(-SiO₃)_x] causes a difference in binding energy of 0.7 eV. This suggests that the two N species are qualitatively distributed in the depth direction: i.e., the difference in the neighboring bonds of nitrogen indicates that the N2 state is dispersed within the SiO₂ matrix in the film, while the N1 state is located at the Si interfacial layers. From a comparison of the above results and reported theoretical expectations for nitrated SiO₂, N3 and N5 can be reliably assigned to O-N=Si₂ and O₂=N-Si species, respectively.⁷ N6 can be assigned to the peak caused by N₂ molecules because the binding energy is very high within the charge screening effect and the N₂, in the gas state, easily diffuses out after the PNA.⁵ Within the above analysis scheme, N4 is left unassigned. Although the nature of the chemical state of N4 cannot be directly assigned, the possible N bonding characteristics could be due to Hf-N bond formation in the matrix of the HfO₂ or a charge screening effect of the N bonding state caused by the SiO₂ fraction that is incorporated in the silicate film.⁸

The most interesting finding regarding the nitrated film is that the higher binding energy states of N4–N6 do not disappear, even after a PNA at 700 °C, although the total quantity of N incorporated into the film is decreased afterward. The composition of the silicate film can critically affect the thermal stability of the chemical state because the N in a film with a high mole fraction of HfO₂ is not stably

maintained in the film, as described in our previous report.^{5,9} Considering the distribution of N1 and N2 in the depth direction, the change in the N1 and N2 peaks after PNA indicates that other unstable bonding states such as Hf–N bonds and interfacial oxidation, which occur during the PNA, are related to the change in N1 and N2.

Figure 2 shows N K edge NEXAFS spectra and Hf 4f core level XPS spectra for 4-nm-thick Hf silicate films containing various fractions of HfO₂. The N K edge of NEXAFS spectra in Hf silicate films show a sharp peak caused by an interstitial N₂ gas component within the HfSiO_xN_y matrix: i.e., the five peaks obtained by high resolution of NEXAFS spectra confirm the presence of N₂ in the molecular state (data not shown here).⁹ The change in the sharp peak height indicates that the quantity of generated N₂ molecules is proportional to the quantity of the HfO₂ fraction in the silicate film, suggesting that the incorporated N bonds more readily to Si, than to Hf, similar to a nitrated silicate film prepared using NH₃ gas.⁵ However, differences in the nitride processes using a nitrogen plasma and NH₃ gas are provided by the Hf 4f XPS core level spectra, as shown in Fig. 2(b). In all samples, it can be seen that the peak is broader than the reported data, which contains some shoulders at a lower binding energy, around 16.5 eV. The peak position at a higher binding energy state indicates that the incorporation of N into the silicate film reduces the ionic bonding characteristics in an opposite manner.⁵ Another Hf 4f peak at 16.5 eV is located at a higher binding energy than the Hf–N binding energy at 15.8 eV reported by Kang *et al.*⁸ The difference in the peak position between our data and previously reported data could be caused by the second nearest neighbors because, if the binding energy of Hf–N is related to the N species with Hf nearest neighbors, the higher bonding characteristics related to Hf–N binding can be differentiated by substituting Hf atoms by O.

The change in stoichiometry of the silicate film in the depth direction was investigated by MEIS spectra, as shown in Fig. 3. The quantity of N in the film containing a high SiO₂ fraction of 70% is higher up to only a few at.% than that of the film with a 30% SiO₂ fraction, which is very different in the case of the thermally nitrated Hf silicate film. When the thermal nitridation process is used, the quantity of N incorporated into the silicate film is totally dependent on

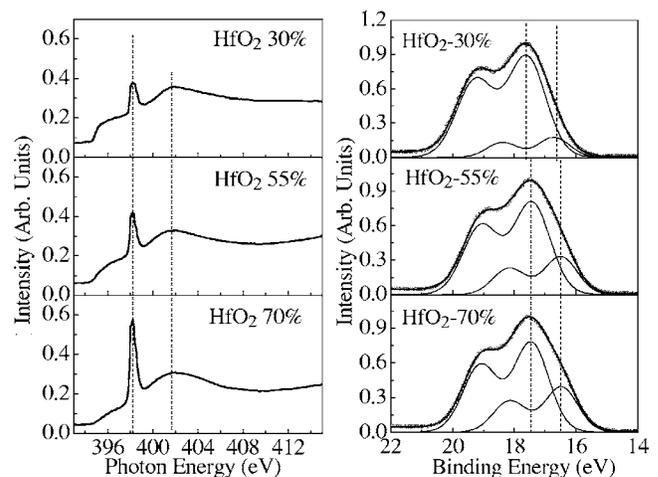


FIG. 2. Left side shows change in the NEXAFS spectra of the N K edge in nitrated Hf silicate films as a function of mole fraction of HfO₂. Right side shows XPS peak spectra of Hf 4f according to HfO₂ mole fractions.

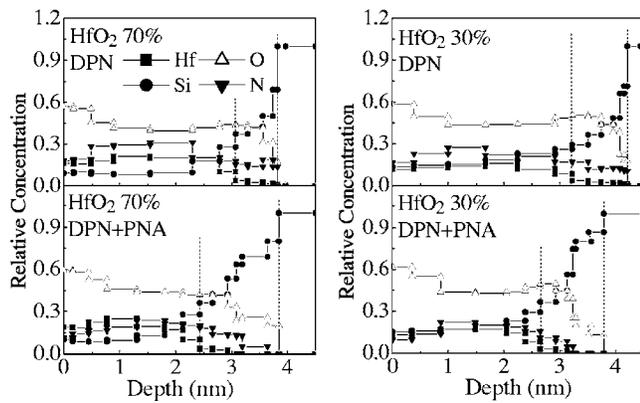


FIG. 3. MEIS spectra for nitrided Hf silicate films with different HfO₂ mole fractions ($x=0.3$ and 0.7). After PNA, the change in composition of the films was also investigated. The relative concentration from the MEIS peak was fitted using the KIDO program.

the fraction of SiO₂, i.e., a much higher quantity of N in a film with a high mole fraction of SiO₂ and a low N content in a film with a low mole fraction of SiO₂.⁵ The difference in the quantity of N in the nitrided films can be related to the high activity of the plasma because a N plasma enhances reactions of N with the film, resulting in a high incorporation of N bonded to Si and even with Hf. Thus, the bonding characteristics resulting from Hf–N and the high quantity incorporated can be attributed to the activity of the plasma. Another interesting finding is that a decrease in thickness and a change in the composition of the film in the depth direction is evident after PNA. In particular, although the thickness of the interfacial layer is increased, that of the film is decreased. During the PNA, reoxidation at the interfacial region and a decrease in the N and Hf contents in the silicate film are observed. In comparing the decrement in the quantity of N in films with different HfO₂ fractions, the N contained in the film with a high HfO₂ fraction is more unstable than that in a film with a low HfO₂ fraction, which is closely related to the thermal stability of N because molecular N₂ and Hf–N bonds are generated to a great extent in a film with a high HfO₂ fraction. Moreover, the oxidation of Si that is dependent on the fraction of Hf can be related to the change in thickness, as reported for the case of the catalytic effect of Hf.¹⁰

Finally, we checked the change in film thickness and bonding characteristics of Hf after PNA using high-resolution transmission electron microscopy (HRTEM) and XPS, respectively, as shown in Fig. 4. The amorphous structure is maintained after PNA because nitridation suppresses crystallization and phase separation. The changes in total film thickness and the interfacial layer are in good agreement with the MEIS results: i.e., MEIS spectra and TEM images shows that the silicate film, not the interfacial layer, is decreased even in a N₂ ambient. Moreover, for the two samples with different HfO₂ fractions, the change in the thickness of the interfacial layer after PNA leads to very different behaviors: i.e., the thickness at the interfacial layer is significantly increased in the sample with a high HfO₂ fraction, while it is slight in the sample with a low HfO₂ fraction. The changes in the quantity of N and Hf in MEIS spectra suggest that the most plausible explanation for this is the thermal stability of Hf–N bonds. That is, in the sample with a high HfO₂ frac-

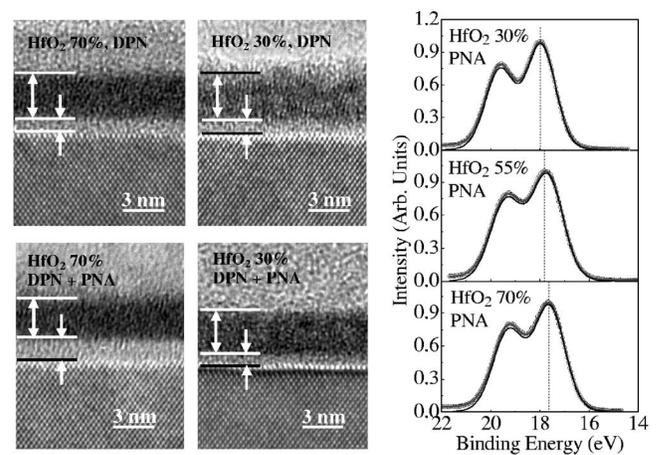


FIG. 4. Left side shows TEM images of nitrided Hf silicate film with different HfO₂ fractions ($x=0.3$ and 0.7). Right side is Hf 4f XPS peak of nitrided Hf silicate film after PNA according to HfO₂ mole fraction.

tion, the decrease in the quantities is larger than that with a low HfO₂ fraction, resulting in a relatively larger decrease in the thickness of the silicate film with a high HfO₂ fraction than that with a low HfO₂ fraction. Unstable H–N bonds can be destroyed during the PNA, some atoms near the destroyed bonds can be affected by the destruction and diffuse out of the sample. The disappearance of the peak caused by Hf–N bonds supports the above possibility, as shown in Fig. 4(b).

In summary, the chemical state of Hf silicate films nitrided by a N plasma was investigated as a function of the mole fraction of HfO₂ and PNA. Peak changes for Hf and N in XPS indicate that N is extensively incorporated into the Hf silicate film; the quantity of the incorporated N is not dependent on the mole fraction of HfO₂ in the silicate film, while the thermal stability of N in the film is critically affected by the mole fraction. Unstable N bonding with Hf is readily destroyed by the PNA, which induces changes in film thickness and composition in the depth direction.

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