

Effects of postnitridation annealing on band gap and band offsets of nitrided Hf-silicate films

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The effects of film composition and postnitridation annealing on band gap and valence band offset were examined in nitrided Hf-silicate films prepared using direct plasma nitridation. Regardless of the composition of Hf-silicate films, the band gap characteristics were similar after direct plasma nitridation (4.5 ± 0.1 eV) and postnitridation annealing (5.6 ± 0.1 eV). The decrease in band gap after direct plasma nitridation was caused by the formation of Si–N and Hf–N bonds, while the recovery of band gap by postnitridation annealing was influenced by the dissociation of unstable Hf–N bonds. The difference in valence band offset was strongly related to the chemical states of Si–N bonds. © 2008 American Institute of Physics. [DOI: 10.1063/1.2826271]

As device size has continued to decrease, oxide materials with high dielectric constants have received considerable attention.¹ Among the numerous high dielectric oxides, Hf-silicate films are attractive candidates to replace the current Si-based gate oxides in complementary metal oxide semiconductor devices. Hf-silicate films offer improved crystallization temperatures and superior thermal stability when in contact with a Si substrate or a poly-Si gate electrode.² Although incorporation of SiO₂ into HfO₂ improves crystallization temperature, Hf-silicate films can readily separate into HfO₂ and SiO₂ above 900 °C because of the large difference in chemical potential between the two oxide phases.³ Recently, N incorporation into Hf-silicate films has been found to improve the thermal stability of the film and to reduce B penetration of the films.⁴ Our previous research showed that phase separation of Hf-silicate films is suppressed by thermal nitridation using NH₃ ambient and by direct plasma nitridation.^{4,5} Moreover, the effects of nitridation on thermal stability are dependent on the nitridation processes, i.e., use of thermal or plasma nitridation. Ikarashi *et al.* found that incorporating N into Hf-silicate films reduced the band gap, which is related to Hf–N coordination.⁶ Sayan *et al.* also observed that nitridation of Hf-silicate films changes the band alignment of the film.⁷ Therefore, understanding the changes in the electronic structure and band structure of Hf-silicate films that result from N incorporation are an important issue because the changes in the band structure, such as the narrowing of band gap, could influence the device performance with the induction of high leakage current. Although previous studies of the nitridation of Hf-silicate films suggest that both the reduction and change in band structure

are caused by N incorporation, the change in band gap and band offset related to the thermal stability of N and to the composition of Hf-silicate films has not been systematically investigated.

The present study focused on the band structure of Hf-silicate films that had been nitrided using direct plasma nitridation (DPN). The changes in band gap and valence band offset related to thermal stability that resulted from N incorporation were examined as a function of composition and postnitridation annealing (PNA) using reflection electron energy loss spectroscopy (REELS) and synchrotron radiation high-resolution x-ray photoelectron spectroscopy (HR-XPS).

The results of the present study indicate that, regardless of the composition of Hf-silicate films, DPN treatment reduces the band gap. The reduction in band gap after DPN treatment is caused by the incorporation of N, which forms Si–N and Hf–N bonds, into the film. The change in valence band offset is dependent on the HfO₂ mole fraction, which is primarily influenced by the chemical states of N in Si-containing compounds, such as Si₃N₄ and (Si₃O)_xN. Moreover, band gap values are restored by PNA treatment primarily due to the diffuse out of unstable Hf–N bonds. The increase in valence band offset, which results from PNA treatment, is critically related to differences in the thermal stability of Si–N bonds, which, in turn, is dependent on the HfO₂ mole fraction.

Metal oxides were grown using atomic layer deposition (ALD) via a vertical, warm-wall reactor with a showerhead and a heated susceptor. Two 3-nm-thick (HfO₂)_x(SiO₂)_{1-x} films on Si of varying composition were prepared using ALD as follows: 30 mol % HfO₂–70 mol % SiO₂ ($x=0.30$), and 70 mol % HfO₂–30 mol % SiO₂ ($x=0.70$). The films were directly nitrided in nitrogen plasma at room temperature and underwent rapid thermal annealing in ambient N₂ at 700 °C for 5 min.

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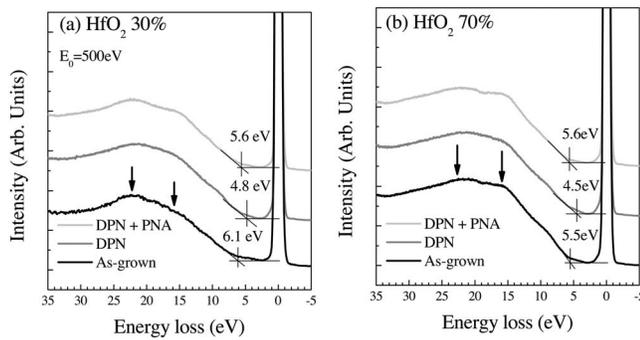


FIG. 1. REELS spectra for Hf-silicate films, using a primary electron energy of 500 eV. (a) HfO₂ 30% and (b) HfO₂ 70%. The band gap energy E_g was defined as the threshold energy of band-to-band excitation. The arrows represent the HfO₂ bulk plasmon peak (~ 16 eV) and the SiO₂ bulk plasmon peak (~ 23 eV), respectively.

To investigate the changes in band gap resulting from DPN and PNA as a function of composition of the Hf-silicate films, electronic structures near the band gap were measured at the atomic level using REELS. Figures 1(a) and 1(b) show the REELS spectra of Hf-silicate films with HfO₂ mole fractions of 30% and 70% after DPN and PNA, respectively. The band gap decreased slightly, from 6.1 ± 0.1 eV to 5.5 ± 0.1 eV, as the HfO₂ mole fraction was increased from 30% to 70%. The Hf-silicate films had two characteristic bulk plasmon peaks due to HfO₂ (~ 16 eV) and SiO₂ (~ 23 eV), as indicated by the arrows in Fig. 1. For the Hf-silicate films with a 30% HfO₂ mole fraction, the SiO₂ bulk plasmon peak around 23 eV exhibited relatively high peak intensity, while for the 70% HfO₂ mole fraction films, the HfO₂ bulk plasmon peak at ~ 16 eV was predominant. The effects of film composition observed in the present study are consistent with our previous study in which the band gap of Hf-silicate films was found to primarily depend on the Hf 5*d* conduction band state and on the O 2*p* valence band state.⁸ The band gap of Hf-silicate films was reduced to 4.6 ± 0.1 eV as a result of DPN treatment and to 4.5 ± 0.1 eV as a function of film composition. The electronic structure near the valence band was affected by N incorporated using DPN treatment because the N 2*p* valence band state can form valence levels higher than the O 2*p* state by approximately 1 eV.⁶ PNA increased the band gap of Hf-silicate thin films by 1.0 eV. The recovery of the band gap to as-grown values may be attributed to the electronic structures that arise from the changes in the chemical state of N. The reduction in band gap after DPN treatment results from N incorporation and the thermal stability of N chemical states is significantly influenced by PNA, based on our previous results.⁵

The valence band offset for Hf-silicate films after DPN and PNA was extracted as a function of film composition, which can be seen in the valence band spectra of the films, as

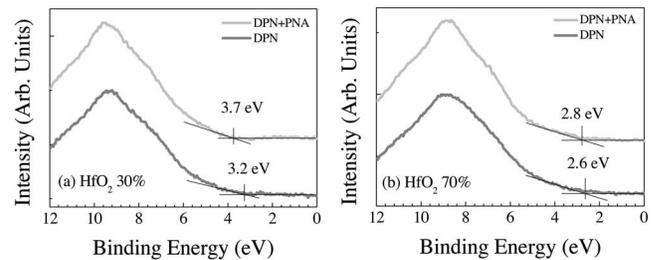


FIG. 2. Valence band spectra for Hf-silicate films. (a) HfO₂ 30% and (b) HfO₂ 70%. The lines describe DPN and DPN+PNA treated films, respectively. The valence band offset energy ΔE_v was defined as the energy difference between the valence band maximum of the dielectrics and that of Si.

shown in Fig. 2. The valence band offset of 30% HfO₂ mole fraction as-grown Hf-silicate films is 3.8 eV and that of the 70% HfO₂ mole fraction films is 3.1 eV based on previous studies.⁸ The difference in the valence band offset between films with different HfO₂ mole fractions may be due to the difference in the O coordination numbers between HfO₂ and SiO₂. After DPN treatment, the valence band offset of Hf-silicate films was dramatically reduced, regardless of film composition, due to the formation of N 2*p* states that are higher than the O 2*p* state. In addition, the PNA process increased the valence band offset. Although the direction of the changes in valence band offset as a function of composition was similar between DPN and PNA treatments, the magnitude of the valence band variation was strongly influenced by film composition. The Hf-silicate films with the higher HfO₂ mole fraction (70%) exhibited large changes in valence band after DPN; however, PNA treatment caused only a slight increase in the valence band offset. In contrast, the valence band offset of the 30% HfO₂ mole fraction Hf-silicate film increased to 3.7 eV, similar to the value of as-grown films. These composition-dependent changes in valence band offset after DPN and PNA treatments indicate that differences in the electronic structure of incorporated N, arising from differences in composition, change the valence band offset.

Table I shows the band gap (E_g) and the valence band offset (ΔE_v) of as-grown Hf-silicate films and nitrided films after DPN and PNA treatments. The band gap was reduced by DPN and recovered by PNA, regardless of the film composition. In both the 30% and 70% HfO₂ mole fraction Hf-silicate films, the valence band offset was dramatically reduced by DPN. After PNA, the valence band offset of the 30% HfO₂ mole fraction Hf-silicate films increased significantly, to values similar to those of as-grown films. However, the valence band offset of the 70% HfO₂ mole fraction films showed a negligible increase. The change in the band alignment was closely related to the changes in conduction band state and valence band state that result from changes in the coordination numbers around each atom. In particular, the

TABLE I. Band gap and valence band offset values for Hf-silicate films as a function of composition and DPN or DPN+PNA treatment.

	As deposited		DPN		DPN+PNA	
	30% HfO ₂	70% HfO ₂	30% HfO ₂	70% HfO ₂	30% HfO ₂	70% HfO ₂
E_g (eV)	6.1	5.5	4.8	4.5	5.6	5.6
ΔE_v (eV)	3.8	3.3	3.2	2.6	3.7	2.8

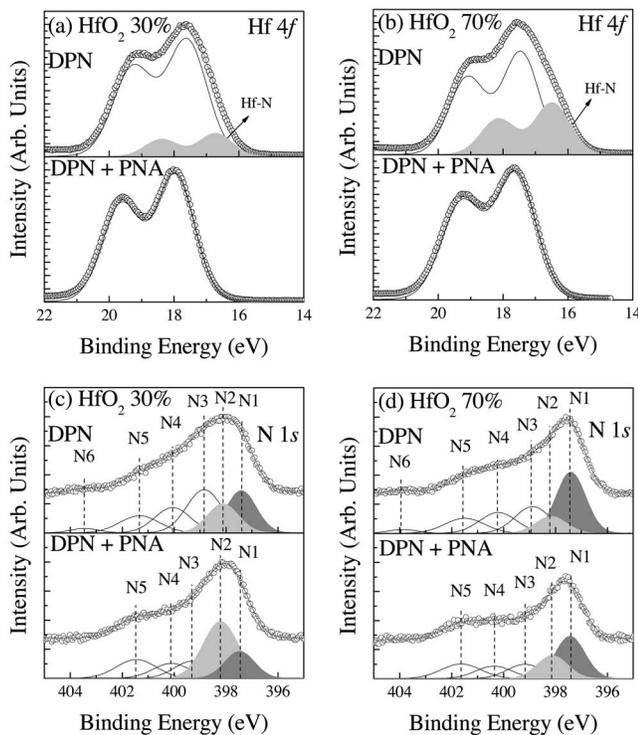


FIG. 3. HR-XPS spectra of Hf $4f$ states (a) HfO₂ 30%, (b) HfO₂ 70% and N $1s$ states, (c) HfO₂ 30%, and (d) HfO₂ 70% measured after DPN and DPN+PNA treatments.

chemical states of N incorporated by DPN play an important role in changing the electronic structure near the band gap.

To characterize N bonding, HR-XPS spectra for Hf $4f$ and N $1s$ were measured after DPN and PNA as a function of composition. The spectra of Hf $4f$ and N $1s$ were deconvoluted into various chemical states using a more detailed analysis. The spectrum of the Hf $4f$ states in Figs. 3(a) and 3(b) resulting from DPN treatment had some shoulders at a lower binding energy (~ 16.5 eV), as shown in our previous report.⁵ This binding energy was assigned to the peak corresponding to Hf–N bonding. The intensity of Hf–N bonding was proportional to the HfO₂ mole fraction in the Hf-silicate films owing to the difference in unbound N and Si as a function of the SiO₂ mole fraction. The Hf–N bonds completely dissociated during PNA at 700 °C. The dissociation of the Hf–N bonds implies that the chemical state of N bound to Hf is very unstable. The N $1s$ peak shown in Figs. 3(c) and 3(d) was deconvoluted into six peaks, considering the nearest N, second nearest N, and neighbors of N from a comparison to previously reported theoretical expectations: following assigned peaks are N1–Si₃N₄; N2–(Si₃O)_xN, N3–Si₂ON, N5–SiO₂N, and N6–N₂.⁹ Within the above consideration of N coordination, the chemical state of N4 could not be directly assigned. The plausible N4 bonding characteristics are related to Hf–N bonding in the matrix of HfO₂, as considered with Hf $4f$ spectra after DPN and PNA.¹⁰ The most important finding was the change between N1 and N2 as a function of the composition and nitridation process. After DPN, the Hf-silicate films with the higher HfO₂ mole fraction had higher intensity N1 states than the films with the lower HfO₂ mole fraction. After PNA, the N2 state drastically increased in the lower HfO₂ mole fraction films. However, the chemical states of N1 and N2 in the higher HfO₂ mole fraction Hf-silicate films were maintained, even though the intensity

of each chemical state decreased slightly. Considering the results of both the band gap and the valence band offset, the changes in the Hf–N and Si–N bonds caused by DPN and PNA treatment imply that the N chemical states are closely related to the band structure of Hf-silicate films. Regardless of the composition, the band gap and the valence band offset of Hf-silicate films were reduced by DPN as the incorporated N formed Si–N and Hf–N bonds. After PNA treatment, the band gap increased, as Hf–N bonds dissociated, independent of film composition. In contrast, the valence band offset of the lower HfO₂ mole fraction film increased to a value of similar to that of as-grown films, while the valence band offset of the higher HfO₂ mole fraction film increased only slightly after PNA. The composition dependence of the change in valence band offset was more closely associated with Si–N bonding than with Hf–N bonding because Hf–N bonds were completely dissociated after PNA. In the lower HfO₂ mole fraction Hf-silicate films, PNA increased the N2 state and decreased the N1 state, leading to an increase in the O $2p$ state and a decrease in the N $2p$ state. The changes in N $2p$ states after PNA could be associated with the slight peak shift of N3 after PNA because of difference of a charge screening effect of N bonding caused by SiO₂ matrix.¹¹ This relative variation in the O $2p$ and N $2p$ states may have an effect on the increase in valence band offset in lower HfO₂ mole fraction Hf-silicate films after PNA. Therefore, band gap is predominantly related to Hf–N bonding, while the valence band offset is affected by changes in Si–N bonding.

In summary, the band alignment evolutions of nitrided Hf-silicate films, prepared using direct plasma nitridation, were investigated as a function of composition and postnitridation annealing. Regardless of the composition of Hf-silicate films, the band gap decreased to $4.5 \text{ eV} \pm 0.1$ after direct plasma nitridation. The band gap was recovered by postnitridation annealing due to the dissociation of unstable Hf–N bonds. However, the change in valence band offset is dependent on the HfO₂ mole fraction, which is primarily influenced by the chemical states of N bonded to Si.

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