Change in band alignment of HfO_2 films with annealing treatments

C. J. Yim and D.-H. Ko[a),b)]
Department of Ceramics Engineering, Yonsei University, Seoul 120-749, Republic of Korea

M. H. Jang, K. B. Chung,[c)] and M.-H. Cho[a),d)]
Institute of Physics and Applied Physics, Yonsei University, Seoul 120-749, Republic of Korea

H. T. Jeon
Department of Material Science and Engineering, Hanyang University, Seoul 133-791, Republic of Korea

(Received 31 August 2007; accepted 29 November 2007; published online 11 January 2008)

Energy band alignment of a nitrided HfO_2 film and dependence of the band gap (E_g) on annealing treatments with nitrogen plasma and ambient gases (N_2 and O_2) were studied by reflection electron energy loss spectra and x-ray photoelectron spectroscopy. We also investigated the nitrogen content in the film and its influence on the band alignment using medium energy ion scattering. The nitrogen incorporated into the HfO_2 film by directed nitrogen plasma treatment significantly decreased the band gap and band offsets, i.e., the incorporated N in the film decreased both conduction and valance band offsets. The nitrogen content in depth direction was dependent on the postannealing conditions using O_2 or N_2. © *2008 American Institute of Physics*. [DOI: 10.1063/1.2826270]

Hf-based oxides have attracted a great deal of interest as gate dielectrics for future metal oxide semiconductor field effect transistor devices because of a suitable dielectric constant, thermal stability with Si, and controllability of the interfacial state. A major challenge for HfO_2 and other high-k dielectric materials is controlling their interface state and trapped charge densities.[1–3] A key to their development is the identification of growth processes for the optimization of oxide bonding within the thin dielectric films at their interfaces. The incorporation of nitrogen has been extensively studied in gate dielectric films including SiO_2 and various high-k films because it plays a key role in present and near-future metal-oxide-semiconductor devices.[4–6]

Although N incorporation is a very promising process for control of interfacial reactions and enhancement of thermal stability of the film, the amount of nitrogen incorporated in HfO_2 is not stably maintained, which critically affects electrical device features.[4,7] Among the electrical device features, the most important characteristics in leakage and reliability of the gate dielectric are basically dependent on the band gap of the film and on band alignment with the Si substrate. This indicates that the incorporation of nitrogen can critically influence characteristics because the incorporated nitrogen affects the electronic structure, which changes both the band gap (E_g) and the band alignment.

In this study, we investigated change in the band gap of nitrided HfO_2 films and band alignment with Si when films were annealed under various conditions. In particular, we focused on changes in the electronic structure and stoichiometry in depth direction of the film after the postannealing treatment in an atmosphere of N_2 and O_2. The stoichiometry in the depth direction was assessed by medium energy ion scattering (MEIS) analysis using H^+ ions with an incident energy of 100 keV. The electronic structure was investigated by near-edge x-ray absorption fine structure (NEXAFS) and x-ray photoelectron spectroscopy (XPS). In order to investigate the E_g for ultrathin dielectric film, reflection energy electron loss spectroscopy (REELS) and spectroscopic ellipsometry (SE) were introduced because REELS effectively reflects the valence and conduction band structures of the samples.[4]

A p-type Si substrate with a resistivity of 2–5 Ω cm was cleaned using the Radio Corporation of America method and the surface oxide was removed by treatment with a dilute HF (1%) solution. Metal oxides were grown using an atomic layer deposition system, which has a vertical warm wall reactor with a shower head and a heated susceptor. HfO_2 films were grown at temperatures below 280 °C using Tetrakis (ethylmethylamido) hafnium as a precursor. H_2O vapor served as the oxygen source and N_2 was supplied as the purge and carrier gas. HfO_2 film thickness was controlled at 30 Å for NEXAFS and REELS measurements. HfO_2 film was nitrided using direct plasma of nitrogen (DPN) at 800 °C. The film was subsequently annealed in either a N_2 (DPNN) or an O_2 atmosphere (DPNO). The band gap changed dramatically with annealing conditions. Moreover, the band alignment with Si was critically affected by the N depth profile in the film.

The changes in the chemical state of HfO_2 as a function of different postannealing processes were examined using XPS, as shown in Fig. 1. Experimentally, the Fermi energy level was determined by measuring the Si $2p_{3/2}$ XPS peak position of the Si and by referencing the peak position of Si with the known Fermi energy. The reported and calculated Fermi energy state of p-Si with a resistivity of 2–5 Ω cm was 98.90 eV±0.1, which is 0.35 eV less than the Fermi energy of intrinsic Si at 99.25 eV.[8,9] The Si $2p$ binding energy of the as-grown HfO_2 on Si was measured at 99.2 eV, as shown in Fig. 1, indicating that band bending occurred near the HfO_2/Si interface of our samples. The increase of the binding energy shows that the difference between the Fermi energy and the valance band maximum is increased near the interface, i.e., the band is bent in the downward direction by as much as 0.3 eV. Moreover, the shift of the Si

[a)]Authors to whom correspondence should be addressed.
[b)]Electronic mail: dhko@yonsei.ac.kr.
[c)]Present address: Department of Physics, North Carolina State University, Raleigh, North Carolina 27695-8202, USA.
[d)]Electronic mail: mh.cho@yonsei.ac.kr.

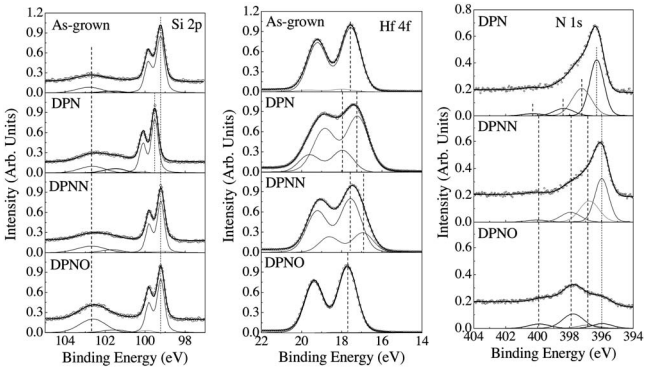

FIG. 1. XPS spectra (a) Si $2p$, (b) Hf $4f$, and (c) N $1s$, as a function of various annealing conditions.

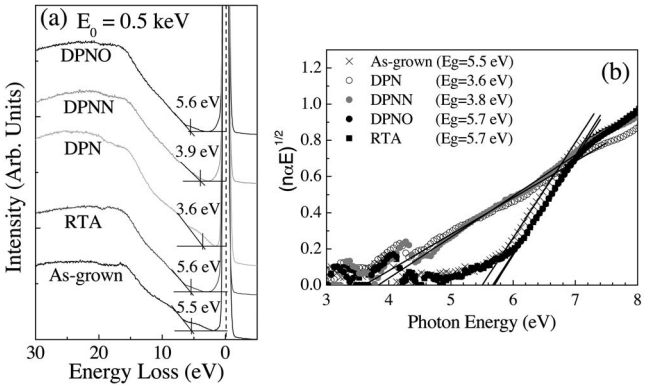

FIG. 2. Reflection electron energy loss spectra (REELS) with different electron gun energies; (a) E_0=0.5 keV. Band gap using (b) spectroscopic ellipsometry is well consistent with the REELS data.

peak to higher binding energy after nitridation of HfO_2/Si shows that band bending further increases to as high as 0.6 eV. Nitridation using direct nitrogen plasma critically affects the electronic structure of HfO_2 film due to the incorporation of N into the film, resulting in the distorted Hf $4f$ peak, compared to the Hf $4f$ peak of as-grown film. The nitrided Hf $4f$ peak is shifted to a lower binding energy due to the decreased ionic bonding characteristics and broadened due to the hybridization of the electronic structure of Hf, resulting in bonding characteristics of Hf–O–N.[4,10] The change in the nitrogen peak as a function of the postannealing condition shows the relationship of nitrogen with the nitrogen bonding with HfO_2. The lower binding energy of the N $1s$ state at 396.3 eV (N1) appears using the DPN process, which is in a very different bonding state than the nitrided HfO_2 using NH_3 gas.[7] The lower binding energy state indicates that the Hf–N bond is formed in the HfO_2 film because the plasma process can more easily nitride the HfO_2 film, even at low temperatures, without any atomic Si transportation. Comparing our previous reported data of the nitridation of HfO_2 film using NH_3 gas, the bonding state at 398.4 eV (N3) can be attributed to nitridation of the HfO_2–SiO_2 complex oxide system.[7] The change in bonding state according to ambient annealing suggests that the chemical state of N located at a lower binding energy is significantly unstable. In particular, in ambient oxygen annealing, the energy state almost disappears, which also reflects the change in the Hf $4f$ peak, remarkably resulting in its dissipation. Thus, we can state that the bonding states of N1 and N2 are related to the bonding between Hf and N. Depending on the ambient condition, the change in band bending is closely related to the change in the interface state rather than to the electronic structure of the film with the quantity of N content because there is no difference in band bending among the postannealing conditions. Moreover, the 0.3 eV band bending after nitridation cannot be caused by the nitrogen content incorporated into the film. During the nitridation process, direct plasma induces accumulated changes at the interface between the film and Si substrate, resulting in moderate damage.[11] A negatively charged state caused by the moderate change at the interface contributes to the band bending downward, as shown in the XPS spectra. During the postannealing treatment, the charged state and carriers are neutralized and removed, resulting in a decrease in band bending.

The energy loss spectrum of O $1s$, which has commonly been used to obtain the band gap, cannot be used to estimate the band-gap energy for HfO_2 film because the core level of Hf $4s$ is located in the vicinity of the loss energy region of O $1s$, which may prevent us from determining E_g through the energy loss spectra for O $1s$. In order to investigate the change of E_g at various annealing conditions without inaccuracy, we used REELS and SE, as shown in Fig 2. The band gap change in SE data is consistent with the change in REELS data at the electron energy of 0.5 keV, which indicates that the SE data critically depended on the absorption condition of the film surface because the incorporated nitrogen is located at the film surface region when using the plasma nitridation process. The electron energy loss spectrum supplies information on the valence and conduction band structure of the samples, i.e., plasmon loss appears below the electron-hole interband transition because the onset of a loss spectrum is due to electron-hole excitation.[12] Thus, we can determine the E_g values from the energy loss signal, which is obtained by drawing a linear fit line with a maximum negative slope from a point near the onset of a loss signal spectrum to the background level, as shown in Fig. 2. For an as-grown HfO_2 film, we can see two significant plasmon peaks near 16 and 9 eV, which correspond to the bulk and surface plasmon peaks of HfO_2, respectively. The measured E_g value from the peak of DPN increases with the incident electron energy, which supports the concept that the nitrogen incorporated into the film is concentrated in the surface region. After nitridation using direct nitrogen plasma, the E_g is drastically decreased to 3.6 eV due to highly incorporated nitrogen, while there is negligible change in E_g caused by crystallization after postannealing treatment using N_2 (RTA). The most important finding is that the change in E_g of the nitrided HfO_2 film is critically dependent on the postannealing circumstance using N_2 or O_2, i.e., E_g is changed to 3.9 and 5.6 eV for N_2 and O_2, respectively. The difference in the changes can be closely related to the quantity of N in the film, as shown in N $1s$ XPS data of Fig. 1.

The XPS valence band spectrum can provide the valance band offset ΔE_v from the energy difference between the valance band minimum (VBM) of the HfO_2 film and the Si substrate, as shown in Fig. 3. The theoretical results predict that the valence band maximum states are composed mostly of the O $2p$ orbital and that the conduction band minimum states are formed mainly by the localized Hf $5d$ orbital for the transitional metal HfO_2.[13,14] Comparing the band alignment of the film with Si, the change in band offset due to HfO_2 nitridation dominantly influences band offsets in val-

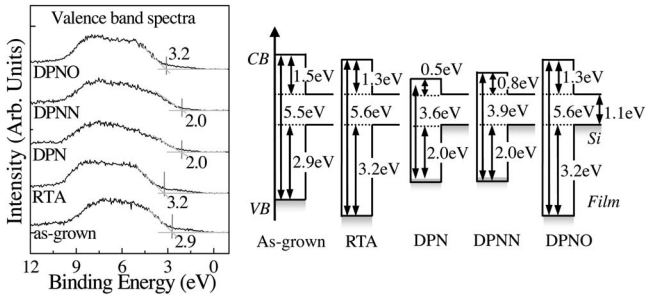

FIG. 3. Valence band spectra for the HfO_2 films (left side) and a band alignment diagram with Si (right side) as a function of various postannealing treatment.

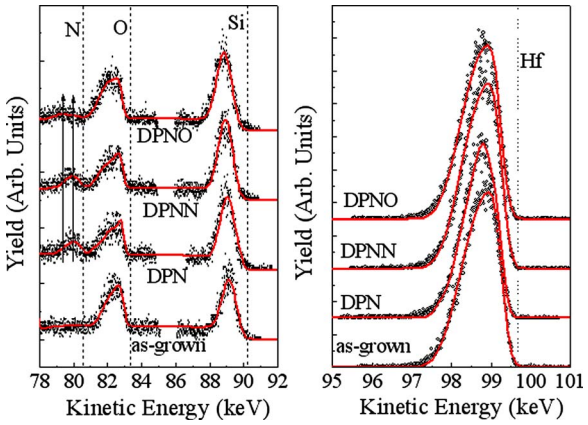

FIG. 4. (Color online) MEIS spectra for a change in concentration in the depth direction as a function of postannealing treatment.

ance and conduction, which differs from the calculated data.[15] Consequently, the change in electronic structure of HfO_2 caused by nitrogen incorporated into the film affects both O $2p$ and Hf $5d$ localized orbitals. The change in E_g and band offset after annealing treatment support the influence of the electronic structure on the band gap and band offset, i.e., under DPNN annealing, the increase in band gap of DPN film fully contributes to the increased band offset in the conduction band but not in the valance band. On the other hand, after DPNO annealing, the band gap is completely recovered to the level of rapid thermal anneal (RTA) film. As shown in the XPS spectra, the decreased bonding state of Hf–N (N1 and N2) can be related to the change in conduction-band offset after DPNN because the slight decrease in the bonding state of Hf $5d$ caused by Hf–N bonding contributes to the change in the conduction band. In contrast, after DPNO, the significant decrease in the quantity of the incorporated N in the film results in an increase in E_g, which almost causes an increase in the valance band. The change in the band offset in the conduction band after DPNO may be related to the crystallization of the film because the change in band offset of crystallized sample DPNO is almost same of that in the crystallized sample RTA, but not in DPN and DPNN.

Finally, we investigated the depth profile of stoichiometry in the nitrided HfO_2 films as a function of annealing. The change in the shape of the Hf peak and the peak position of nitrogen in the nitrided HfO_2 film shows that some O are exchanged with N during the nitrogen plasma process and that nitrogen is more concentrated on the surface of the HfO_2 film than at the interfacial layer (Fig. 4). After annealing in ambient N_2, most nitrogen is still observed, although some portion of nitrogen in the film surface is decreased. On the other hand, after annealing in ambient O_2, almost all nitrogen disappeared from the film. Moreover, the peak change in O and N shows that N is exchanged with O during DPNO. This suggests that the exchange of N with O can cause the change in both electronic structure of Hf $5d$ and O $2p$ states, resulting in both the increase of valance and the conduction band of the film. Inversely, during the nitridation process, the incorporated N also changes both electronic structures, resulting in a decrease of both band offsets.

In summary, we have reported a change in E_g and band offset of nitrided HfO_2 film and the relationship of E_g and band offset with various postannealing treatments on nitrided HfO_2 film. The band gap and band offsets are significantly changed with the quantity of nitrogen incorporated into the film, which is explained by the change in electronic structure of the nitrided HfO_2 film. The postnitridation annealing process critically influences the change in the electronic structure of the film related to the N-bonding state. In particular, the DPNO process reoxidizes the film through the exchange of N with O, resulting in recovering E_g and band offset.

This work was partially supported by the National Program for Tera-level Nanodevices of the Ministry of Science and Technology as one of the 21 Century Frontier Programs. We gratefully acknowledge the technical advice of K. Chae, C. C. Hwang, and H.-N. Hwang at PAL on beamline 7B1.

[1] G. D. Wilk, R. M. Wallace, and J. M. Anthony, Appl. Phys. Lett. **76**, 112 (2000).
[2] E. Gusev, D. A. Buchanan, and E. Cartier, Tech. Dig. - Int. Electron Devices Meet. **2001**, 451.
[3] B. Guillaumot, X. Garros, F. Lime, K. Oshima, B. Tavel, J. A. Chroboczek, P. Masson, R. Truche, A. M. Papon, F. Martin, J. F. Damlencourt, S. Maitrejean, M. Rivoire, C. Leroux, S. Cristoloveanu, G. Ghibaudo, J. L. Autran, T. Skotnicki, and S. Deleonibus, Tech. Dig. - Int. Electron Devices Meet. **2002**, 355.
[4] C. H. Choi, S. J. Rhee, T. S. Jeon, N. Lu, J. H. Sim, R. Clark, M. Niwa, and D. L. Kwong, Tech. Dig. - Int. Electron Devices Meet. **2002**, 857.
[5] H. N. Alshareef, H. Niimi, A. Varghese, M. Bavan, R. Kuan, J. Holt, P. Tiner, and R. Khamankar, Appl. Phys. Lett. **86**, 132901 (2005).
[6] H. Kim, P. C. McIntyre, C. O. Chui, K. C. Saraswat, and M.-H. Cho, Appl. Phys. Lett. **85**, 2902 (2004).
[7] M.-H. Cho, K. B. Chung, C. N. Whang, D.-H. Ko, J. H. Lee, and N. I. Lee, Appl. Phys. Lett. **88**, 202902 (2006).
[8] L. J. Huang and W. M. Lau, Appl. Phys. Lett. **60**, 1108 (1992).
[9] W. Song, M. Yoshitake, R. Tan, and I. Kojima, Appl. Surf. Sci. **253**, 3508 (2007).
[10] 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).
[11] I. J. Baumvol, C. Krug, F. C. Stedile, M. L. Green, D. C. Jacobson, D. Eaglesham, J. D. Bernstein, J. Shao, A. S. Denholm, and P. L. Kellerman, Appl. Phys. Lett. **74**, 806 (1999).
[12] P. Poveda and A. Glachant, Surf. Sci. **323**, 258 (1995).
[13] R. S. Johnson, Y. Zhang, and J. L. Whitten, Appl. Phys. Lett. **79**, 1775 (2001).
[14] N. T. Barrett, O. Renault, P. Besson, Y. Le Tiec, and F. Martin, Appl. Phys. Lett. **88**, 162906 (2006).
[15] G. Shang, P. W. Peacock, and J. Robertson, Appl. Phys. Lett. **84**, 106 (2004).