Changes in the structure of an atomic-layer-deposited HfO_2 film on a GaAs (100) substrate as a function of postannealing temperature

C. Y. Kim,[1] S. W. Cho,[1] M.-H. Cho,[1,a)] K. B. Chung,[2] D. C. Suh,[3] D.-H. Ko,[3] C.-H. An,[4] H. Kim,[4] and H. J. Lee[4]
[1]*Institute of Physics and Applied Physics, Yonsei University, Seoul 120-749, Republic of Korea*
[2]*Department of Physics, North Carolina State University, Raleigh, North Carolina 27695-8202, USA*
[3]*Department of Material Science and Engineering, Yonsei University, Seoul 120-749, Republic of Korea*
[4]*School of Materials Science and Engineering, Sungkyunkwan University, Suwon 440-746, Republic of Korea*

(Received 30 March 2009; accepted 24 June 2009; published online 28 July 2009)

The effects of postannealing temperature on the crystal structure and energy band gap (E_g) values of atomic-layer-deposited HfO_2 films grown on a GaAs (100) substrate were investigated. In postannealed HfO_2 films prepared using a rapid thermal annealing (RTA) process in a N_2 ambient at temperatures over 600 °C, the initially produced, partially crystallized HfO_2 film changed into a well-ordered crystalline structure with no detectable interfacial layer between the film and the GaAs substrate. In the case of a RTA prepared at 700 °C, the thickness of the film was relatively increased compared to that of an as-grown film. Changes in the depth profile data related to stoichiometry and electronic structure after the annealing treatment indicated that Ga oxide is formed within the HfO_2 film during the RTA. The formation of Ga oxide in the film significantly affected the E_g values, i.e., the E_g changed from 5.5 for an as-grown film to 4.7 eV for a film annealed at 700 °C. © *2009 American Institute of Physics*. [DOI: 10.1063/1.3182702]

The employment of high carrier transport semiconductors such as strained SiGe, Ge, and III-V based semiconductors has been a subject of considerable interest from researchers in the device industries as well as in academia.[1–3] In order to develop a strategy for preparing a high performance MOS device, the combination of HfO_2 and GaAs as a high carrier transport substrate has been seriously considered because hafnium oxide (HfO_2) as a gate dielectric material has a suitable dielectric constant, a wide band gap, and acceptable thermal stability.[4] Kim *et al.*[5] estimated the electrical performance of HfO_2 as gate dielectric material on GaAs in a MOS field effect transistor. Hinkle *et al.*[6] reported on the utility of an atomic-layer deposition (ALD) process in the growth of HfO_2 on a GaAs substrate, which provides information concerning the selection of appropriate surface treatments and ALD precursors. In order to enhance the performance of HfO_2/GaAs-based MOS applications, a more detailed understanding of the structural characteristics related to the gate leakage current and energy band gap is needed (E_g).[7] Such structural characteristics of the metal oxide are closely related to thermodynamic properties such as the reactivity of the interface between high-κ metal oxides/high mobility substrates.

In this study, we focused on changes in the structural characteristics and energy band gap (E_g) values in an ALD HfO_2/GaAs film as a function of postannealing temperature. Partially crystallized HfO_2 films were found to be converted into a well-ordered crystalline structure after an postannealing process in a N_2 ambient at 600 °C. For the case of a film postannealed at 700 °C, the formation of Ga oxide within the HfO_2 film was observed, although the well-ordered crystalline structure continues to be maintained. Moreover, the E_g value was significantly decreased from 5.5 eV for an as-grown film to 4.7 eV for a film annealed at 700 °C. These results show that interfacial reactions between HfO_2 and GaAs have a substantial influence on the change in crystalline structure as well as the E_g values.

A Si-doped *n*-type GaAs (100) substrate with a doping concentration of 1×10^{-18} cm^{-3} was cleaned using the chemical etching method. Prior to the deposition of HfO_2, the cleaned GaAs surface was subjected to a wet chemical etch with a buffed oxide etching (BOE) (NH_4F:Hf=6:1) solution for 20 min. 3.5-nm-thick HfO_2 films were immediately grown on the GaAs surface at a temperature of 290 °C using an ALD system. This rapid thermal annealing (RTA) of HfO_2/GaAs films was carried out for 1 min in a N_2 ambient at 600 and 700 °C, respectively. The structural characteristics and electronic structure of the HfO_2 films on GaAs were investigated by high resolution transmission electron microscopy (HRTEM) and the near-edge x-ray adsorption fine structure (NEXAFS) examined using a synchrotron x-ray source at the Pohang accelerator laboratory on beam-line 7B1. Elemental composition was determined by medium energy ion spectroscopy (MEIS). The value of the energy band gaps in the HfO_2/GaAs was determined by reflection electron energy loss spectroscopy (REELS).

Figure 1 shows cross-sectional HRTEM images of a 3.5-nm-thick ALD HfO_2 film grown on cleaned GaAs substrates. The HRTEM images show relatively sharp interfaces below an approximately 1-nm-thick interface between HfO_2 and GaAs, compared to previously reported data for ALD HfO_2/GaAs films that were produced by removing native oxides using a surface treatment with BOE and a self-cleaning ALD process.[8] The most interesting finding is that the partially crystallized HfO_2 film on GaAs was converted into a well-ordered crystal structure after the RTA at 600 °C. The abrupt interface without any detectable interface layer

a)Author to whom correspondence should be addressed. Electronic mail: mh.cho@yonsei.ac.kr.

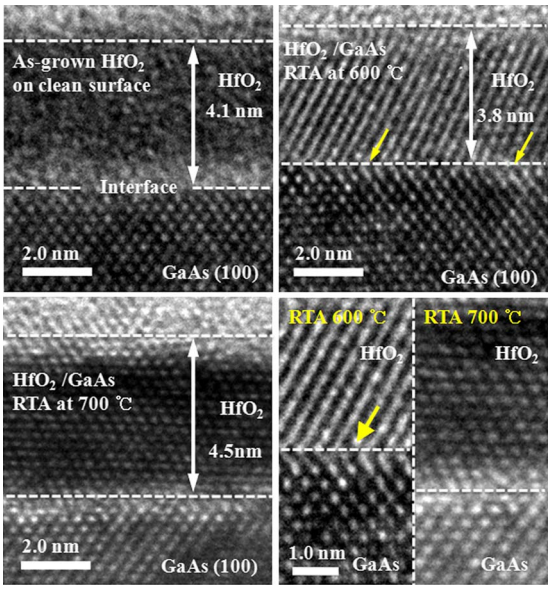

FIG. 1. (Color online) HRTEM images of HfO_2 films on a BOE treated GaAs (100) surface are shown along the GaAs [110] direction. The image shows changes in the crystal structure from an amorphous to a crystalline phase during postannealing processes at 600 °C. The arrows represent the lattice mismatch for interfacial atoms between the HfO_2 film and the GaAs substrate.

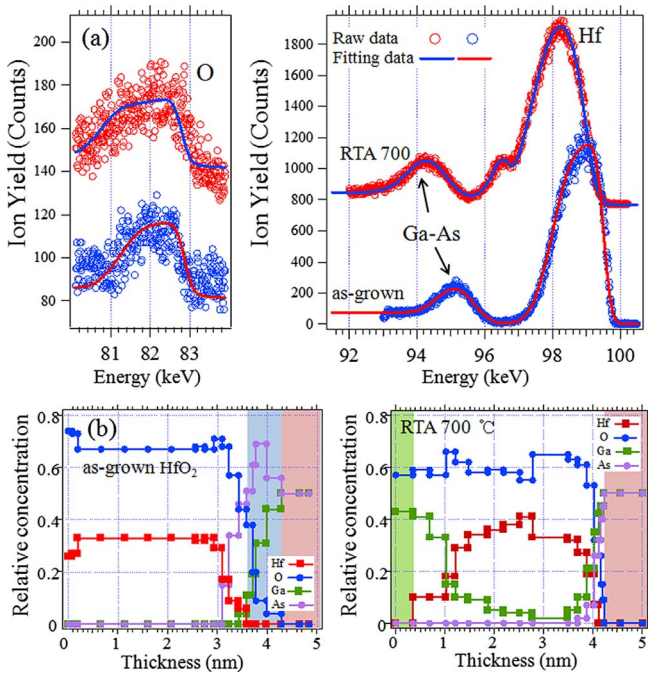

FIG. 2. (Color online) (a) Hf, Ga–As, and O peaks of measured MEIS spectra and (b) compositional depth profiles for 4-nm-thick HfO_2/GaAs films as a function of postannealing temperature. The Ga and As peaks were observed as one peak, in which the Ga and As peaks are overlapped, due to the similarity of each atomic mass.

continues to be maintained. This observation indicates that a suitable annealing temperature constitutes a key parameter in constructing a crystalline HfO_2 film on a GaAs substrate, i.e., the energy barrier for crystallization can be overcome by supplying sufficient kinetic energy, resulting in a well-ordered crystalline HfO_2 film on GaAs, which is similar to that obtained by solid-phase epitaxy induced by an annealing process. The atomic arrangement between the HfO_2 film and the GaAs adopts a periodic iteration via a solid phase epitaxial reaction, thus minimizing interfacial lattice mismatch, i.e., 12 atoms in the HfO_2 film on 11 atoms in the GaAs substrate, a periodic iteration. In this system, the HfO_2 film adopts a monoclinic rather than a tetragonal phase because changing the phase transformation to a tetragonal phase requires a higher annealing temperature. Considering the lattice constant of 5.175 Å for the *b*-axis in monoclinic HfO_2 and that of 5.653 Å in zincblende GaAs, this arrangement shows that the lattice mismatch can be minimized to 0.133%, resulting in minimal interfacial strain.[7] After the RTA at 700 °C, however, no critical change in the crystalline structure of the HfO_2 film is observed and the abrupt interface between the HfO_2/GaAs continues to be maintained. However, the thickness of the film became thicker, reaching 4.5 nm. We analyzed elemental composition and depth profiles for samples in detail. MEIS measurements were employed to verify the increased thickness and the characteristics of the crystallized HfO_2 films as a function of postannealing temperature.

Figure 2 shows the measured MEIS spectra for the Hf, Ga–As, and O peaks and compositional depth profiles for an as-grown film and for the RTA at 700 °C, respectively. The most interesting finding is that there are significant differences in the shape of the spectra, the peak width, and the position of the Hf, Ga–As, and O peaks between two films, as shown in Fig. 2(a). After the RTA treatment, the increase in the intensity of the Hf peak width is associated with the increased thickness of the HfO_2 film. The leading edge of the Ga–As peak in the RTA sample is shifted to a greater extent toward the lower scattering energy than that of the as-grown sample due to beam energy losses, as the result of the increase in the thickness of the HfO_2 film during the MEIS process. This result is in good agreement and consistent with the HRTEM results. In particular, the shoulder of the Hf peak at 96.5 keV is generated and the leading edge of the Hf peak near a scattering energy of 99 keV after the RTA treatment was shifted toward a lower scattering energy of about 0.5 keV, compared to that of the as-grown film. This result is closely related to the formation of the surface layer, i.e., the compositional depth profile of Fig. 2(b) indicates that Ga oxide is formed by out-diffusion from an interfacial region to the surface region of the HfO_2 film. The distinct shoulder at the lower energy edge of Hf peak and fitted data are clearly consistent with the formation of surface Ga oxide [inset of Fig. 2(a)]. Considering the thermodynamic data for the Ga oxide, $3O_2+GaAs \rightarrow Ga_2O_3$ $(-1089\ J/k\ mol)+4As$, it is possible to form a Ga oxide layer at the HfO_2/GaAs interface. In the crystallization process of HfO_2 during the RTA process, Ga_2O_3 can diffuse to the surface region of the HfO_2 and some of the resulting Ga_2O_3 is incorporated into the HfO_2 film, which leads to the increased thickness of the film.[9,10]

In order to investigate changes in the molecular structure that are related to crystallization and the electronic structure in the HfO_2 film, NEXAFS and x-ray photoelectron spectroscopy (XPS) were conducted. Figure 3 shows O *K*-edge data for NEXAFS and the Hf 4*f* core-level energy state in XPS as a function of postannealing temperature. In Fig. 3(a), the O *K*-edge absorption spectra of the HfO_2 film are deconvoluted into two absorption peaks at ~533 eV (e_g) and ~537 eV (t_{2g}), respectively.[11] The next three unoccupied orbital states

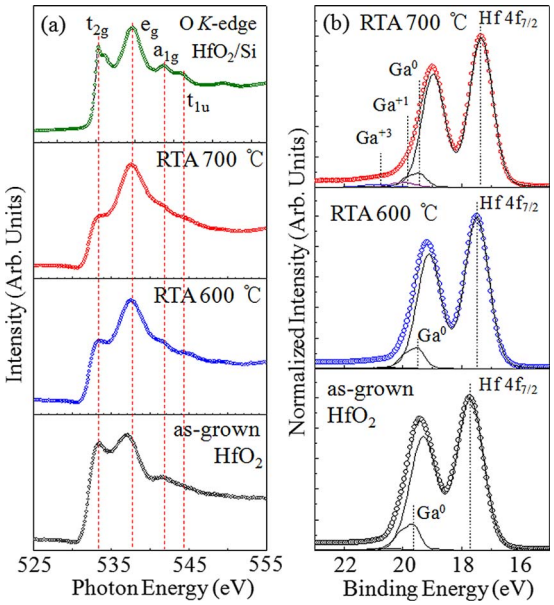

FIG. 3. (Color online) (a) NEXAFS spectra of the O *K* edge features for HfO2/GaAs films. The O *K*-edge features of the NEXAFS spectra in the HfO_2 films were changed after the postannealing treatments. (b) Hf 4*f* core-level spectra for HfO2/GaAs films were measured by XPS as a function of postannealing temperature.

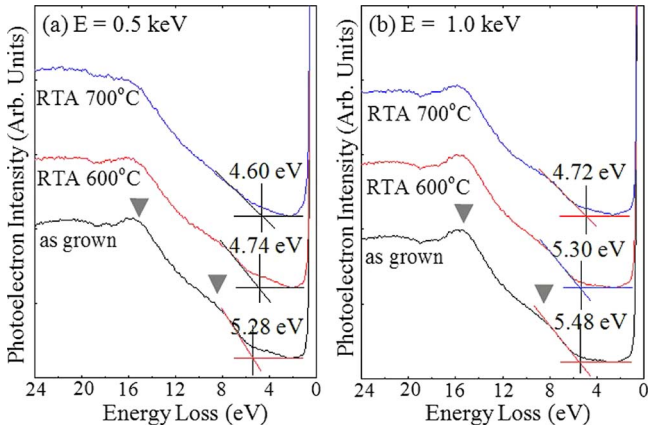

FIG. 4. (Color online) REELS spectra for HfO_2/GaAs films as function of postannealing temperature, using an incident electron energy of 1.0 keV. The E_g values were defined as the threshold energy of band-to-band excitation. The arrows represent the HfO_2 surface plasmon peak near 9 eV and the bulk plasmon peak near 16 eV, respectively.

clearly appeared at the higher energy region of 540 (a_{1g}) and 542 eV (t_{1u}), which are associated with hybridization between the O 2*p* and Hf 6*s* and 6*p* states in the molecular structure of crystallized HfO_2.[11] To investigate this issue more closely, we prepared crystalline HfO_2/Si as an alternate sample to confirm the NEXAFS spectra of crystallized HfO_2. An interesting observation is that the NEXAFS spectra of HfO_2/GaAs after RTA are very different from that for HfO_2/Si, as shown by the HRTEM results in Fig. 1. As the annealing temperature is increased from 600 to 700 °C, the t_{2g} and e_g components in the absorption spectra gradually became broadened. The spectrum of Ga_2O_3 has a double band caused by hybridized O *p* states with Ga 4*sp* states. Thus, the relatively high peak intensity of t_{2g} and e_g in the film grown on GaAs is caused by the formation Ga_2O_3 during the annealing treatment. Moreover, the peak change indicates that the formation of Ga_2O_3 in HfO_2 increases with increasing annealing temperature. Another important finding is shown in the XPS spectra of Hf 4*f*, as shown in Fig. 3(b), i.e., the change in the Hf 4*f* peak shows that two peaks are present and are due to the presence of Ga from GaAs and Ga oxide in the peak. The peak change for Ga is caused by the increased formation of Ga_2O_3, while the width of the Hf 4*f* peak gradually decreases with increasing annealing temperature, indicating that no chemical interactions occur between HfO_2 and Ga_2O_3. Finally, the increase in the thickness of the HfO_2 film after annealing treatment at 700 °C can be attributed to the incorporation of Ga_2O_3 into HfO_2.

The values of the energy band gaps (E_g) for HfO_2/GaAs as a function of postannealing temperature, as shown in Fig. 4, were determined by REELS.[12] In order to obtain E_g values for the HfO_2 films grown on GaAs in the depth direction, the incident electron energy was controlled from 0.5 to 1.0 keV. The most interesting finding is the decrease in E_g values after the postannealing processes, i.e., the E_g value for the as-grown film was determined to be 5.5 eV, while the E_g values for the film that had been post-treated at 700 °C was decreased up to 4.7 eV. The E_g value of 4.7 eV is consistent with the reported E_g value for Ga oxide.[13] This decrease in E_g can be understood by considering the formation of Ga oxides within and/or on the HfO_2 films, as indicated by the MEIS and NEXAFS results.

In conclusion, well-ordered crystalline HfO_2 films on GaAs were produced when a postannealing temperature of over 600 °C was used. During the annealing process, interfacial Ga oxide diffuses to the film surface. The E_g value of 5.5 eV for as-grown HfO_2 film gradually decreases to 4.72 eV as the annealing temperature increases to 700 °C. The changes in film thickness and the reduction in E_g values are closely dependent on the formation of Ga oxides within the HfO_2 film.

This work is partially supported by the IT R&D program of MKE/IITA (Grant No. 2008-F-023-01, next generation future device fabricated by using nanojunction) and System IC 2010 project of the Korea Ministry of Science and Technology and Ministry of Commerce, Industry and Energy.

[1] M.-H. Cho, H. S. Chang, D. W. Moon, S. K. Kang, B. K. Min, D.-H. Ko, H. S. Kim, and P. C. McIntyre, Appl. Phys. Lett. **84**, 1171 (2004).
[2] M. Perego, G. Seguini, and M. Fanciulli, J. Appl. Phys. **100**, 093718 (2006).
[3] G. Seguini, M. Perego, S. Spoga, A. Dimoulas, and M. Fanciulli, Appl. Phys. Lett. **91**, 192902 (2007).
[4] K. B. Chung, U. Hwang, H. J. Kang, D. C. Suh, H. C. Sohn, D.-H. Ko, S. H. Kim, H. T. Jeon, and M.-H. Cho, Appl. Phys. Lett. **92**, 022907 (2008).
[5] H.-S. Kim, I. Ok, M. Zhang, F. Zhu, S. Park, J. Yum, H. Zhao, and J. C. Lee, Appl. Phys. Lett. **92**, 032907 (2008).
[6] C. L. Hinkle, A. M. Sonnet, E. M. Vogel, S. McDonnell, G. J. Hughes, M. Milojevic, B. Lee, F. S. Aguirre-Tostado, K. J. Choi, H. C. Kim, J. Kim, and R. M. Wallace, Appl. Phys. Lett. **92**, 071901 (2008).
[7] X. Zhao and D. Vanderbilt, Phys. Rev. B **65**, 233106 (2002).
[8] J. C. Hackley, J. D. Demaree, and T. Gougousi, Appl. Phys. Lett. **92**, 162902 (2008).
[9] H. S. Chang, H. Hwang, Mann-ho Cho, H. K. Kim, and D. Won Moon, J. Vac. Sci. Technol. A **22**, 165 (2004).
[10] P. Kruse, J. G. McLean, and A. Kummel, J. Chem. Phys. **113**, 9217 (2000).
[11] D. H. Hill, R. A. Bartynski, N. V. Nguyen, A. C. Davydov, D. Chandler-Horowitz, and M. M. Frank, J. Appl. Phys. **103**, 093712 (2008).
[12] Y. Kamimuta, M. Koike, T. Ino, M. Suzuki, M. Koyama, Y. Tsunashima, and A. Nishiyama, Jpn. J. Appl. Phys., Part 1 **44**, 1301 (2005).
[13] J. Robertson and B. Falabretti, J. Appl. Phys. **100**, 014111 (2006).