Effect of interfacial reactions between atomic-layer-deposited HfO₂ films and *n*-GaAs ⟨100⟩ substrate using postnitridation with NH₃ vapor

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Using a variety of various physical measurements, the effects of postnitridation annealing using NH₃ vapor on the interface between atomic-layer-deposited HfO₂ films and *n*-GaAs (100) substrates were investigated. After the nitridation treatment, from x-ray absorption spectroscopy and high resolution x-ray photoemission spectroscopy data indicate that the incorporation of Ga oxides into HfO₂ films was significantly suppressed during the annealing treatment, primarily because of chemical reactions at the interface between Ga_2O_3 and NH₃. Microstructural analyses further confirmed that the HfO₂ film was fully crystallized and a thin GaO_xN_y layer had been formed at the HfO₂/GaAs interface during the annealing process. Compared with the energy band alignments before and after the annealing process, the valence band offsets and energy band gaps were not changed substantially, because the interfacial nitride layer effectively blocked the diffusion of Ga oxide into the film. © *2010 American Institute of Physics*. [doi:10.1063/1.3481801]

Because of the continuous need to scale gate length in complementary metal-oxide-semiconductor (MOS) development, advanced gate stack structures based on high-κ metal oxides and high mobility III-V compound semiconductor substrates have been a subject of extensive investigation.[1,2] Among advanced gate stack structures, HfO₂/GaAs (or $In_xGa_{1-x}As$) structure is currently considered to be one of the plausible solutions for next generation MOS applications. Such a structure offers a number of advantages in electric properties, leading to higher density integration, low leakage current, shorter switching speed, and lower power consumption.[3,4] Despite such promising properties in MOS applications, the adoption of a HfO₂/GaAs structure has many drawbacks in terms of applications to apply to future device structures due to the lack of a stable interface oxide and an inherently lower thermal budget.[5] In this regard, several efforts to achieve high-quality HfO₂/GaAs interfaces have involved the use of an interfacial self-cleaning effect during the preparation of atomic-layer-deposited (ALD) high-κ metal oxides.[5,6] Although the interfacial self-cleaning effect during the ALD process considerably consumes some of the initial native oxides on GaAs surface, the interface oxides (especially Ga oxides) at a high-κ/GaAs interface cannot be completely removed.[5,6] Our previously reported findings indicate that Ga oxides formed at the HfO₂/GaAs interface diffuse into the HfO₂ film during the postannealing treatment.[5,7]

In this study, we focused on the influence of postdeposition nitridation (PDN) using NH₃ vapor on the electronic structures, chemical bonding states, and crystal structures at the interface between ALD HfO₂ films and *n*-GaAs (100) substrates. For PDN samples, the crystal field (CF) splitting

on unoccupied states in the O K_1-edge absorption spectra of HfO₂/GaAs was clearly observed by x-ray absorption spectroscopy. This can be attributed to the suppression of Ga oxide formation in HfO₂ films, because chemical reactions between interfacial Ga_2O_3 and NH₃ vapor lead to the formation of a GaO_xN_y interface layer. This reaction was confirmed by high resolution x-ray photoelectron spectroscopy (HRXPS). Through microstructural analysis, we also ob-
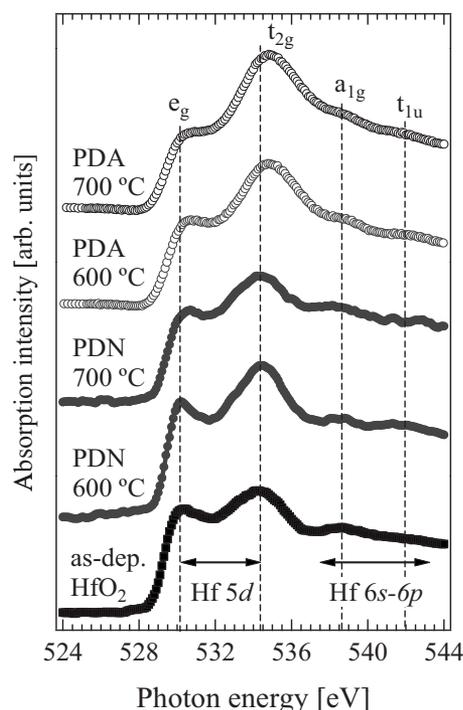

FIG. 1. O K_1-edge absorption spectra in XAS results for HfO₂/GaAs films. MO structure of monoclinic HfO₂ film was assigned to a sevenfold oxygen coordination on the basis of a cubic symmetry.

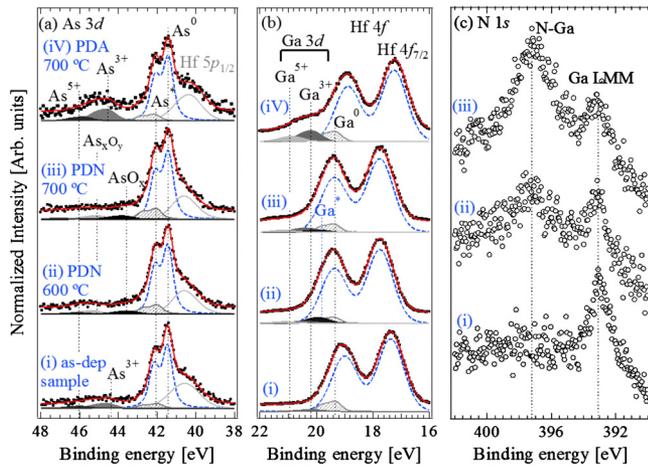a)Author to whom correspondence should be addressed. Electronic mail: mh.cho@yonsei.ac.kr.

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FIG. 2. (Color online) XPS core-level spectra of HfO_2 films grown on n-GaAs: (a) As $3d$, (b) Hf $4f$/Ga $3d$, and (c) N $1s$ core-level spectra were also obtained as a function of postannealing ambient and temperature. In As $3d$ XPS spectra, As^0, As^*, As^{+3}, and As^{+5} bonding states corresponding to bulk GaAs, elemental As, As_2O_3, and As_2O_5 states, respectively. In Hf $4f$/Ga $3d$ spectra, Ga, Ga^{+3}, and Ga^{+5} bonding states corresponded to bulk GaAs, Ga_2O_3, and Ga_2O_5 states, respectively. Ga^* bonding represents Ga–O–N bonding states, due to the intermediate state of GaN with the reaction of Ga_2O_3 and NH_3.

served that the HfO_2 films on GaAs were fully crystallized after PDN and that a thin interfacial layer corresponding to GaO_xN_y was formed as well. Finally, we investigated the band alignment of HfO_2/GaAs before and after PDN, and no significant changes were found. This suggests that interfacial nitride layer suppresses the formation of Ga–O in HfO_2 films.

Prior to the deposition of HfO_2 films, the n-type GaAs (100) substrates were cleaned using a chemical etching method with a buffed oxide etching (NH_4F:HF=6:1) solution. 4.0 nm thick HfO_2 films were immediately grown on the GaAs surface at a substrate temperature of 320 °C using an ALD system, with tetrakis (ethylmethylamido) hafnium as the precursor and H_2O vapor as the oxygen source. The film thickness of the HfO_2 film was confirmed by high-resolution transmission electron microscopy (HRTEM). By using two alternative annealing procedures, i.e., NH_3 (PDN) and a N_2 [postdeposition annealing (PDA)] ambient, the effects of postannealing treatments on HfO_2/GaAs were investigated for a rapid thermal treatment for 1 min at 600 °C and 700 °C, respectively. X-ray adsorption spectroscopy (XAS) measurements were performed using a synchrotron x-ray source at the Pohang accelerator laboratory on beam-line 7B1, and the molecular orbital (MO) structures on the con-
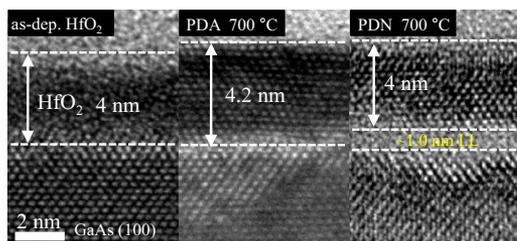

FIG. 3. (Color online) HRTEM images of HfO_2 films on an n-GaAs (100) surface are shown along the GaAs (110) direction. The image shows changes in the crystal structure from an amorphous to a crystalline phase after PDA and PDN at 600 °C, respectively. In the case of PDN, the thickness of the GaO_xN_y layer is estimated to be approximately 1.0 nm.

duction band of HfO_2/GaAs were clearly observed. The chemical structures in HfO_2/GaAs in both the PDN and PDA samples were investigated using HRXPS with a mono-chromatic Al $K\alpha$ x-ray source ($h\nu$=1486.6 eV), at the Korea Basic Science Institute in Jeonju. In order to verify the changes in MO features, the structural characteristics of the HfO_2/GaAs films were analyzed by HRTEM as well. To compare band alignments between the PDN and PDA samples, the values for the energy band gaps in the HfO_2/GaAs were determined by reflection electron energy loss spectroscopy (REELS) in which the primary beam energy was 1.0 keV.

The MO structures of the conduction band in the HfO_2 films grown on a n-GaAs (100) substrate via XAS were measured as a function of postannealing ambient and processing temperature, as shown in Fig. 1. The O K_1-edge absorption spectrum represents the hybridized MOs between Hf with $5d$, $6s$, and $6p$ and O with $2p$ states, which are based on the local bonding symmetry.[8–10] Interestingly, for both PDN and PDA treated HfO_2/GaAs samples, four distinct absorption peaks were observed in O K_1-edge spectra, leading to the CF splitting in the MO structure of HfO_2. Through our previous XAS study, it is obvious that the spectral changes in O K_1-edge peaks are closely related to a change in the crystallization of HfO_2 films grown on GaAs.[7,11] Hence, HfO_2 films nitrided with NH_3 were crystallized, similar to the PDA treatment. With increasing annealing temperature, differences between the PDA and PDN samples were observed in the Hf $5d$ e_g and t_{2g} state features in O K_1-edge peaks: i.e., the Hf $5d$ t_{2g} states of the PDA sample were shifted to higher photon energy than that of the as-deposited sample, while no change was observed for the PDN sample. After PDA, furthermore, absorption peaks caused by CF splitting in HfO_2/GaAs became weakened significantly as the result of the incorporation Ga–O into the HfO_2 film.[7] In turn, Ga $4sp$ of the Ga–O incorporated in HfO_2 film was simultaneously detected in the Hf $5d$ peaks of the XAS spectrum. Even though four absorption peaks associated with Hf states are slightly weakened as the PDN temperature was increased up to 700 °C, these absorption peaks were distinctly deconvoluted, as shown in Fig. 1. As a result, this suggests that the PDN treatment can sufficiently suppress the diffusion of Ga–O into the film.

HRXPS measurements were carried out in order to investigate changes in the chemical bonding states at the HfO_2/GaAs interface. Figures 2(a)–2(c) show the As $3d$, Hf $4f$/Ga $3d$, and N $1s$ core-level spectra as a function of postdeposition temperature, respectively. As shown in Figs. 2(a) and 2(b), the As $3d$ and Ga $3d$ spectra for the as-deposited HfO_2/GaAs sample indicate that As–O and Ga–O bonding states can be detected. The interesting finding is that the spectral changes in the As–O states of As $3d$ spectra and the Ga–O states of the Ga $3d$ spectra are significantly dependent, not only on the annealing temperature, but also on annealing ambient. After PDA treatment at 700 °C, the intensities of the As–O states increase significantly, due to re-oxidation processes between elemental As and diffused impurities during the PDA. On the other hand, as the PDN temperature is increased up to 700 °C, the As–O states are gradually decomposed and nonstoichiometric As oxides (AsO_x and As_xO_y) and elemental As (As^0) are generated. This indicates that thermal desorption of the As–O states

TABLE I. Summary of band alignment for HfO$_2$ films grown on n-GaAs in terms of postannealing ambient and temperature. The valence band offsets (ΔE_V) and band gaps (E_g) were obtained by HRXPS and REELS, respectively. During REELS, we collected the electron beam energy at 1.0 keV.

Samples		As-dep. HfO$_2$ film	With postannealing in N$_2$ vapor		With postnitridation in NH$_3$ vapor	
			600 °C	700 °C	600 °C	700 °C
Band alignment	ΔE_V (eV $\pm$ 0.1)	2.54	2.53	2.54	2.44	2.47
	E_g (eV $\pm$ 0.1)	5.51	5.30	4.72	5.50	5.45

proceeds continuously, while the reoxidation process is relatively suppressed during the PDN treatment. In addition, the intensities of the Ga–O bonding states (Ga^{3+} and Ga^{5+}) are significantly increased after the PDA at 700 °C,[7] while the formation of Ga oxides was significantly inhibited during PDN up to 700 °C, as shown in Fig. 2(b). In Fig. 2(c), as the PDN temperature is increased up to 700 °C, the relative amount of nitrogen content in N 1s spectra increase gradually, which is consistent with Ga–O–N bonding states at 397.2 eV.[12] Thus, the suppression of the formation Ga oxides can be attributed to the formation of an interfacial GaO$_x$N$_y$ layer (Ga–O–N:Ga*, 19.8 eV) because the subsequent reaction between Ga oxide states and NH$_3$ at HfO$_2$/GaAs interface is possible at temperatures over 600 °C (Ref. 13)

$$Ga_2O_{3(s)} + 2NH_{3(g)} \rightarrow 2GaN_{(s)} + 3H_2O_{(g)}.$$
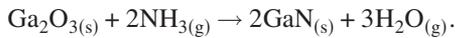
The cross-sectional HRTEM analyses were performed to confirm the changes in MO structures and the interfacial reaction in HfO$_2$/GaAs after the PDN treatment, as shown in Fig. 3. The thickness of the as-deposited HfO$_2$ films was estimated to be 4 nm and this thickness was maintained for both PDN and PDA treatments for temperatures of up to 600 °C (not shown here). A noteworthy finding is that the interfacial characteristics between a HfO$_2$ film and GaAs substrate are dependent on the postannealing ambient: i.e., an abrupt interface between HfO$_2$ film and GaAs substrate was observed after PDA treatments, while a thin interfacial layer ($\sim$1 nm) was formed after the PDN treatments. The interfacial layer is caused by the GaO$_x$N$_y$ layer formed by the nitridation process using NH$_3$ vapor, as evidenced by the HRXPS results. Moreover, the thickness of the HfO$_2$ film after PDA at 700 °C became thicker than that of an as-deposited HfO$_2$ film, while the film thickness was maintained during the PDN treatment at 700 °C. The relative change in thickness reflects the fact that the GaO$_x$N$_y$ layer effectively suppresses the diffusion of Ga into the HfO$_2$ film. Interestingly, although a thin amorphous GaO$_x$N$_y$ layer is formed at the interface between HfO$_2$/GaAs after a PDN treatment at 600 °C, the resulting HfO$_2$ film was fully crystallized.

For both the PDN and PDA treatments, we measured the band alignments of HfO$_2$/GaAs, so as to investigate the effect of the interfacial reaction, and the results are summarized in Table I. The valence band offsets (ΔE_V) and energy band gaps (E_g) for post-treated HfO$_2$/GaAs samples were measured using HRXPS and REELS, respectively. For as-deposited HfO$_2$/GaAs, the ΔE_V and E_g were estimated to be 2.54 $\pm$ 0.1 eV and 5.51 $\pm$ 0.1 eV, respectively, consistent with previous reported values for the band alignment in ALD-HfO$_2$ on GaAs.[2,7] The ΔE_V values in HfO$_2$/GaAs were unchanged after the annealing treatments in the two different ambient conditions, while the E_g values in HfO$_2$ films were dependent on the ambient and temperature dependences.

When the PDA temperature was increased up to 700 °C, the E_g values gradually decreased from 5.5 to 4.7 eV. On the other hand, when the PDN temperature was increased up to 700 °C, the E_g values remained at approximately 5.5 eV. This can be understood by considering that the Ga oxides formed in HfO$_2$ films: i.e., the out diffusion of Ga–O is effectively suppressed in the PDN treatment due to the formation of a thin GaO$_x$N$_y$ layer at the HfO$_2$/GaAs interface.

In conclusion, we examined the effect of PDN with NH$_3$ vapor on HfO$_2$/GaAs films, using a variety of various physical measurements. Through the combined application of XAS and HRXPS, we confirmed that, after PDN, the out diffusion of Ga–O into the HfO$_2$ film is suppressed via the formation of a GaO$_x$N$_y$ layer at the HfO$_2$/GaAs interface. Furthermore, HRTEM images show that a partially crystallized HfO$_2$ film is transformed into a highly ordered crystalline phase after PDN and confirm the formation of a thin GaO$_x$N$_y$ layer. Finally, before and after PDN, the values of the valence band offsets and E_g remain constant due to the suppression of Ga oxide formation in the HfO$_2$ film. The findings reported herein suggest that the nature of the HfO$_2$/GaAs interface can be controlled by the formation of a thin GaO$_x$N$_y$ layer when an appropriate postnitridation with NH$_3$ vapor is used.

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