

Interfacial reaction of atomic-layer-deposited HfO₂ film as a function of the surface state of an *n*-GaAs (100) substrate

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The characteristics of interfacial reactions and the valence band offset of HfO₂ films grown on GaAs by atomic layer deposition were investigated by combining high-resolution x-ray photoelectron spectroscopy and high-resolution electron transmission microscopy. The interfacial characteristics are significantly dependent on the surface state of the GaAs substrate. Polycrystalline HfO₂ film on a clean GaAs surface was changed to a well-ordered crystalline film as the annealing temperature increased, and a clean interface with no interfacial layer formed at temperatures above 600 °C. The valence band offset of the film grown on the oxidized GaAs surface gradually increased with the stoichiometric change in the interfacial layer. © 2008 American Institute of Physics.

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With Si-based metal-oxide-semiconductor (MOS) devices beginning to show limits in physical and electrical properties, there have been tremendous efforts in research to develop an innovative MOS structure using innovative materials for high-performance applications. The employment of semiconductor material with high carrier transport properties, such as strained SiGe, Ge, and III-V-based semiconductors, has received intensive attention from device researchers in both industry and academia.¹⁻⁴ Although applying semiconductor material as a substrate has the potential for advanced device performance, the lack of a stable oxide on the substrates has impeded application to MOS devices due to poor qualities of the interface, such as high defect states and Fermi-level pinning. In particular, GaAs has attracted a lot of recent interest due to its possible application to high-speed and low-power MOS application using high-*k* dielectrics.

In this letter, we examine the band alignment caused by the interfacial reaction of ALD-HfO₂ films on GaAs as a function of the surface conditions of a GaAs substrate. In addition, thermal annealing effects on the interfacial characteristics of an HfO₂/GaAs system were investigated using high-resolution x-ray photoelectron spectroscopy (HRXPS) and high-resolution transmission electron microscopy (HR-TEM) after postdeposition annealing at various temperatures. The results of this study indicate that the changes in interfacial reactions and band alignments are critically dependent on the thermal stability of the film.

N-type, Si-doped GaAs (100) substrates with a doping concentration of $1 \times 10^{18} \text{ cm}^{-3}$ were treated with two different surface passivation methods prior to HfO₂ deposition to compare interfacial characteristics: wet chemical etch and plasma oxidation. For chemical etching, all of the GaAs substrates were cleaned using a buffed oxide etchant (BOE)

(NH₄F:HF=6:1) solution for 20 min (S1). Some samples were oxidized using plasma for 5 min at 300 °C (S2). Using an ALD system, 4-nm-thick HfO₂ films were immediately grown onto each GaAs substrate at a temperature of 290 °C. Tetrakis (ethylmethylamido) hafnium and H₂O vapor were used as reacting precursors, and N₂ was used as the purge and carrier gas. Rapid thermal annealing was carried out on the selected samples at 600 and 700 °C for 1 min under a N₂ ambient. The chemical bonding characteristics and the valence band offset (VBO) were evaluated by HRXPS using a monochromatic Al *K*α (1486.7 eV) with a pass energy of 20 eV under a base pressure of 1×10^{-9} torr.

Using HRXPS, changes in the chemical bonding states of HfO₂/GaAs samples were investigated as a function of the different surface conditions. Figure 1 shows the As 3*d* and Ga 3*d* core level spectra of the GaAs substrates with and without HfO₂ films following different surface passivation techniques. As 3*d* spectra in S2 clearly showed As–Ga, As⁺³, and As⁺⁵ bonding states, respectively.⁵ In the case of S1, we observed only the As⁺³ state due to the formation of As₂O₃, while in S2 two clear oxidized states, As⁺³ and As⁺⁵, resulted from the formation of As₂O₃ and As₂O₅, respectively. These results can be explained by Gibbs energy of formation data, which states that the formation of As₂O₃ is preferable to that of As₂O₅, when the energy per atom is considered.⁶ Both oxidized states of As⁺³ and As⁺⁵ were significantly decreased during the HfO₂ growth on both surfaces. The decrease in the quantity of oxidation states after ALD growth implies that the interfacial layer was critically affected by the condition of surface treatment: i.e., the interfacial oxide layer caused by oxidation of the As atom was completely removed in the S1 sample, while some was observed in sample S2 after the ALD-HfO₂ growth. Because surface cleaning is known to act on the surface oxide top layer via the self-cleaning effect,⁶ ideally, the surface oxide layer should be completely removed during the initial growth stage of HfO₂. However, the data show that the surface oxide is not com-

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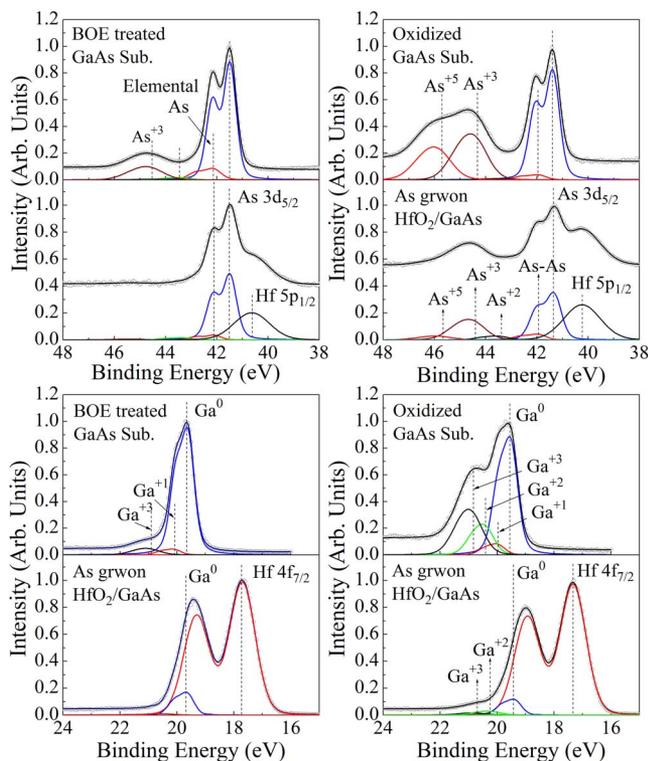


FIG. 1. (Color online) The XPS spectra of BOE-treated GaAs(left side) and oxidized GaAs (right side): the upper line is As $3d$ and the lower line is Ga $3d$. XPS spectra were also obtained for the film grown on the surfaces. In As $3d$ spectra, As–Ga, As^{+3} , and As^{+5} bonding states corresponded to binding energies at 41.4, 44.3, and 45.5 eV, respectively. In Ga $3d$ spectra, Ga^{+1} , Ga^{+2} , and Ga^{+3} bonding states corresponded to binding energies at 20.0, 20.4, and 20.8 eV, respectively. A Hf $5p$ peak due to Hf–O bonding was observed at a binding energy of 40.3 eV, slightly overlapping the As peaks.

pletely removed when it is at a certain thickness (~ 2 nm). The difference in the quantities of As_2O_3 and As_2O_5 was nearly the same before and after ALD growth, indicating that there was no preference in selective etching between the oxides. Thus, the steric hindrance effect can be expected to play a significant role in the ALD process during the self-cleaning process, thereby failing to remove the entire oxide layer.⁶ The Ga–O feature also has multiple oxidation states, which includes Ga^{+1} , Ga^{+2} , and Ga^{+3} , due to the formation of Ga_2O , GaO (H), and Ga_2O_3 , respectively,⁷ which were used to deconvolute the Ga–O peaks. After ALD growth, we obtained changes in the Ga–O bonding states that were very similar to those of As–O: the Ga–O bonding states were nearly re-

moved on the BOE-treated surface, while they were still observed on the oxidized surface after the ALD growth.

The intensities of deconvoluted peaks for As and Ga are summarized in Table I. The most interesting finding is that, after the postdeposition annealing process in an N_2 ambient, there was no significant change in the chemical bonding states of the HfO_2 film grown on S1, which resulted in a suppression of the interfacial reaction between the HfO_2 film and the substrate. On the other hand, the change in the chemical bonding states of the HfO_2 film grown on S2 was more complex after the annealing treatment. Comparing the As state of the as-grown film with that of the annealed film, the As^{+3} state was significantly decreased after annealing at 600 °C. The change in the Ga–O state, in particular, the increase in the Ga^{+3} state due to the formation of Ga_2O_3 , clearly explains the changes in the As and Ga states. Another interesting finding is that the change in full width at half maximum of the Hf peak was also affected by the condition of the GaAs surface, which can be related to the structural characteristics.⁸

The structural changes in the HfO_2 /GaAs samples under different surface treatment conditions were investigated using HRTEM, as shown in Fig. 2. The most important finding is that an abrupt interface with no observable interfacial layer formed in the HfO_2 sample on S1 after postdeposition annealing at 600 °C. The polycrystalline structure was changed to a fairly well-ordered crystalline structure on S1, while the polycrystalline structure was still observed on S2. The abrupt interface indicated that there was no formation of an interfacial layer due to the reaction between the GaAs surface and the HfO_2 film, which is in good agreement with the previously discussed changes in the XPS peaks of Ga $3d$ and As $3d$. However, the interfacial layer still was observed in the annealed film grown on the oxidized surface, although the interfacial layer had slightly decreased due to the reaction process of Ga_2O_3 and As_2O_3 , as shown in the XPS data of Fig. 1 and Table I. The thermodynamic data on the chemical reaction, $As_2O_3 + 2GaAs \rightarrow Ga_2O_3 + 4As$ ($\Delta G = -62$ kcal/mol),⁵ indicate that the formation of Ga_2O_3 was favored and that As_2O_3 was deoxidized, which is consistent with the gradual increment in the formation of Ga_2O_3 after annealing treatment. From XPS and HRTEM, it would be reasonable to assume that some of the deoxidized As atom was reoxidized at the annealing temperature due to the oxygen present in the inert N_2 ambient, and that some of the oxidized As molecules were diffused through the film as a gaseous state. As a result, the change in the interfacial

TABLE I. Changes in the normalized intensities in several kinds of arsenic and gallium oxides for HfO_2 with S1 and S2. The peaks of As and Ga were normalized with the As substrate peak (As^0) and the Hf peak, respectively. As^{+1} , As^{+2} , As^{+3} , and As^{+5} bonding states corresponded to As_2O , AsO, As_2O_3 , and As_2O_5 , respectively. Ga^{+1} , Ga^{+2} , and Ga^{+3} corresponded to Ga_2O , GaO(H), Ga_2O_3 , and Ga_2O_3 , respectively.

Samples	Annealing temperature (°C)	Arsenic oxides				Gallium oxides		
		As^{+1}	As^{+2}	As^{+3}	As^{+5}	Ga^{+1}	Ga^{+2}	Ga^{+3}
S1	As grown	...	0.016
	600	0.010
	700	0.010	0.012	0.020	...	0.013
S2	As grown	0.015	0.028	0.153	0.028	...	0.029	0.016
	600	0.020	0.010	0.033	0.019	0.026	0.014	0.045
	700	0.023	0.014	0.051	0.034	0.025	0.025	0.079

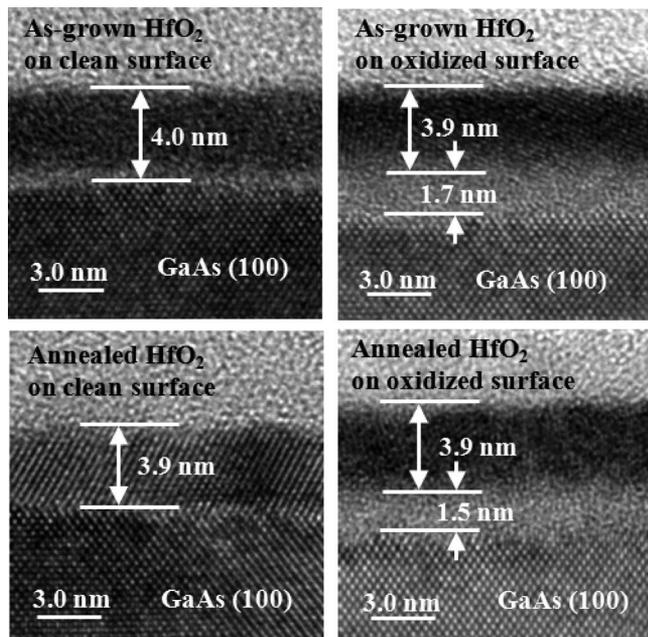


FIG. 2. HRTEM images of HfO₂ films grown on BOE-treated GaAs (left side) and oxidized GaAs (right side). The images of the films annealed at 600 °C were also obtained.

layers of TEM and XPS shows that the stoichiometry of the interfacial layer had changed from As₂O₃ to Ga₂O₃ as a main composition before and after annealing treatment, respectively.

The valence band spectra in the XPS data provided the values of VBOs on the energy level difference for the GaAs substrate and the valence band maximum (VBM) in HfO₂ film, as shown in Fig. 3. We found clear differences in the films on the surfaces; the interface Fermi energy was observed at 0.78 eV for the film grown on the oxidized surface and at 0.84 eV for the film on the BOE-treated surface. Kobayahi *et al.* reported that the interface Fermi level is estimated to be 0.85 eV above the VBM when considering that the bulk Fermi level is located 0.03 eV below the conduction-band minimum.⁹ The most important finding is that the change in the VBO was dependent on the surface

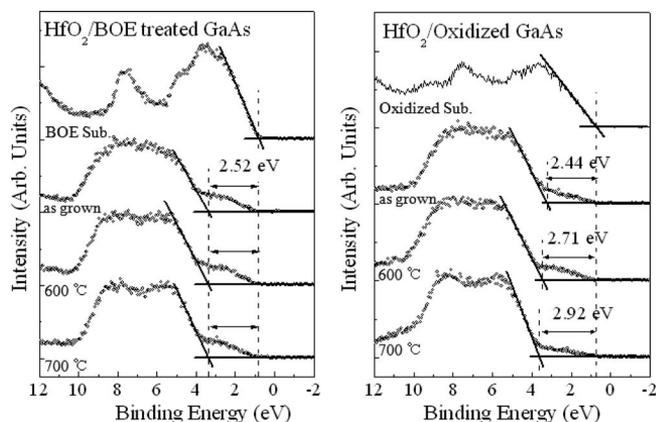


FIG. 3. Valence band data of HfO₂/GaAs films. The Fermi energy did not change with annealing temperatures up to 700 °C. The VBO on BOE-treated surface was not changed, while it on oxidized surface increased as the annealing temperature increased.

condition of GaAs—i.e., the VBO of the film grown on the oxidized surface gradually increased, while that on the BOE-treated surface was unchanged, as the annealing temperature increased up to 700 °C. The measured VBO value of the as-grown film, compared with the reported value of 2.3 eV, is in good agreement and is within the experimental margin of error.³ Moreover, the increase in value can be associated with the interfacial reaction after the annealing treatment, as shown in the previous XPS data—i.e., there is no change in the VBO of the film on S1, while there is change in the value of the film on S2 after the annealing treatment. In both cases, during postannealing treatments, the change in the shape of the valence band spectra was similar to that of gallium oxide formed within the HfO₂ films,^{5,9} and was closely related to the crystallization of the films after the postannealing processes.¹⁰ The change in VBO was consistent with the change in the Ga³⁺ state in our XPS results. Thus, in HfO₂/S2, the interfacial Ga oxides affected the VBO considerably, resulting in an increase in VBO from 2.4 to 2.9 eV, while, in the S1 case, the value of VBO was mainly determined by the valence band spectra of HfO₂ due to the lack of interfacial oxide. The increment in VBO can be understood by the effect of the increase in the Ga oxide layer thickness at the interface between HfO₂/GaAs, which is consistent with the theoretical report by Robertson *et al.* that the band offsets of high- κ oxides/high mobility substrates can be increased due to the interfacial oxide layer.¹¹

In summary, we report a change in the interfacial reaction of a HfO₂ film on a GaAs substrate, as well as a change in its VBO value as a function of surface treatment conditions and postannealing treatment. An abrupt interface with no interfacial layer and good crystalline structure was obtained in the film grown on a BOE-treated surface. Moreover, the VBO was affected by the change in the interfacial oxide layer, resulting in a gradual increase in the VBO as the annealing temperature increased.

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