

## GaAs interfacial self-cleaning by atomic layer deposition

C. L. Hinkle,<sup>1,a)</sup> A. M. Sonnet,<sup>1</sup> E. M. Vogel,<sup>1,2,b)</sup> S. McDonnell,<sup>3</sup> G. J. Hughes,<sup>3</sup> M. Milojevic,<sup>2</sup> B. Lee,<sup>2</sup> F. S. Aguirre-Tostado,<sup>2</sup> K. J. Choi,<sup>2</sup> H. C. Kim,<sup>2</sup> J. Kim,<sup>2</sup> and R. M. Wallace<sup>2,c)</sup>

<sup>1</sup>Department of Electrical Engineering, The University of Texas at Dallas, Richardson, Texas 75080, USA

<sup>2</sup>Materials Science and Engineering, The University of Texas at Dallas, Richardson, Texas 75080, USA

<sup>3</sup>School of Physical Sciences, Dublin City University, Glasnevin, Dublin 9, Ireland

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The reduction and removal of surface oxides from GaAs substrates by atomic layer deposition (ALD) of Al<sub>2</sub>O<sub>3</sub> and HfO<sub>2</sub> are studied using *in situ* monochromatic x-ray photoelectron spectroscopy. Using the combination of *in situ* deposition and analysis techniques, the interfacial “self-cleaning” is shown to be oxidation state dependent as well as metal organic precursor dependent. Thermodynamics, charge balance, and oxygen coordination drive the removal of certain species of surface oxides while allowing others to remain. These factors suggest proper selection of surface treatments and ALD precursors can result in selective interfacial bonding arrangements.

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The removal of oxides at the GaAs/dielectric interface has been shown recently to be critical for the reduction of accumulation capacitance frequency dispersion in GaAs metal oxide semiconductor capacitors.<sup>1</sup> Previous *ex situ* studies of Al<sub>2</sub>O<sub>3</sub> and HfO<sub>2</sub> atomic layer deposition (ALD) on GaAs and InGaAs have reported an interfacial “self-cleaning” reaction process that effectively reduces As and Ga oxide thin films. Ye *et al.* and later Frank *et al.* reported a reduction in interfacial oxides using trimethylaluminum (TMA) as the precursor<sup>2</sup> for Al<sub>2</sub>O<sub>3</sub> as well as no interfacial oxide reduction using HfCl<sub>4</sub> as the precursor for HfO<sub>2</sub> ALD films<sup>3</sup> at 300 °C. Dalapati *et al.* reported that some remnant oxides are detected after similar ALD processes at 300 °C.<sup>4</sup> Huang *et al.*<sup>5</sup> and Chang *et al.*<sup>6</sup> have reported the removal of As oxides on InGaAs using Al<sub>2</sub>O<sub>3</sub> (TMA) and HfO<sub>2</sub> [tetrakis (ethylmethylamino) hafnium (TEMA-Hf)], respectively. Shahrjerdi *et al.*<sup>7</sup> reported no self-cleaning using tetrakis (dimethyl-amino) hafnium on GaAs. In this letter, monochromatic x-ray photoelectron spectroscopy (XPS) is used to study the interfacial characteristics of *in situ* ALD Al<sub>2</sub>O<sub>3</sub> and HfO<sub>2</sub> deposition on GaAs surfaces to provide a fundamental understanding of interfacial self-cleaning. The *in situ* capabilities allow for a detailed analysis (e.g., oxidation state dependence) of the self-cleaning and reveal contrasting results to *ex situ* studies.

The samples used in this work were *n*-type Si-doped GaAs wafers with doping concentration of  $5 \times 10^{17} \text{ cm}^{-3}$ . Two alternative GaAs starting surfaces were used in this study. The first were native oxides on GaAs that were taken directly out of the sealed wafer holders sent by the GaAs wafer supplier. The other GaAs surfaces were prepared by degreasing the wafers in acetone, methanol, and isopropyl alcohol for 1 min each, followed by a 3 min etch in 29% NH<sub>4</sub>OH.<sup>8</sup> *In situ* Al<sub>2</sub>O<sub>3</sub> and HfO<sub>2</sub> thin films were deposited on GaAs in a Picosun ALD reactor integrated to a UHV multitechnique deposition/characterization system (base

pressure =  $2 \times 10^{-11}$  mbar) (Ref. 9) at a substrate temperature of 300 °C and a base pressure of  $\sim 700$  mTorr. TMA and TEMA-Hf, delivered through heated lines/valves, were used as the metal organic precursors for Al<sub>2</sub>O<sub>3</sub> and HfO<sub>2</sub> formation, respectively. The oxygen source was de-ionized H<sub>2</sub>O. The metal organic was the first precursor pulse followed by the H<sub>2</sub>O to complete one cycle (1 cycle  $\approx 0.1$  nm). Analysis of the deposited films was done using an *in situ* monochromatic XPS using an Al K $\alpha$  (1486.7 eV) x-ray source with a linewidth of  $\sim 0.25$  eV and pass energy of 15 eV.

Figure 1(a) shows the As 2*p* spectra of the native oxide covered GaAs samples and subsequent 1 nm depositions of the high-*k* dielectrics. The native oxide of GaAs has two As oxidation states, As<sup>3+</sup> and As<sup>5+</sup>, corresponding to As<sub>2</sub>O<sub>3</sub> and As<sub>2</sub>O<sub>5</sub>, respectively.<sup>10</sup> The top plot shows a peak around 1326.5 eV corresponding to the convolution of the two As oxide peaks. These peaks have been assigned based on previous studies of GaAs oxides grown by air exposure, chemical, and thermal means.<sup>10–12</sup> After 1 nm Al<sub>2</sub>O<sub>3</sub> deposition, the As oxide peak is greatly reduced and can be fit with only the As<sup>5+</sup> oxidation state feature. Exposure to the TMA precursor with H<sub>2</sub>O at 300 °C results in the reduction of the As<sup>3+</sup> oxidation state intensity to below XPS detectable limits, consistent with previous reports.<sup>2,3,6</sup> In contrast, after 1 nm HfO<sub>2</sub> deposition, the As<sup>5+</sup> oxidation state intensity has been reduced, while a remnant As<sup>3+</sup> state intensity remains. Recent studies by our group have shown that it is in fact the metal-organic precursor half-cycle (and not the subsequent oxidation with H<sub>2</sub>O) which removes the native oxides and most of the reduction occurs during the first TMA pulse.<sup>13</sup>

Figure 1(b) shows the Ga 2*p* spectra for the same native oxide covered sample and subsequent high-*k* depositions. The Ga–O feature also has multiple oxidation states including Ga<sup>3+</sup> and Ga<sup>5+</sup> as well as other oxide species probably including Ga<sub>2</sub>O, GaO<sub>2</sub>, and Ga suboxides as well as GaAsO<sub>4</sub>.<sup>12</sup> These additional oxidation states make the quantitative deconvolution of the Ga–O feature more difficult than for the As–O feature. Despite this difficulty, it is still possible to determine some qualitative trends due to the interfacial self-cleaning. It is important to point out that while

<sup>a)</sup>Electronic mail: chris.hinkle@utdallas.edu.

<sup>b)</sup>Electronic mail: eric.vogel@utdallas.edu.

<sup>c)</sup>Electronic mail: rmwallace@utdallas.edu.

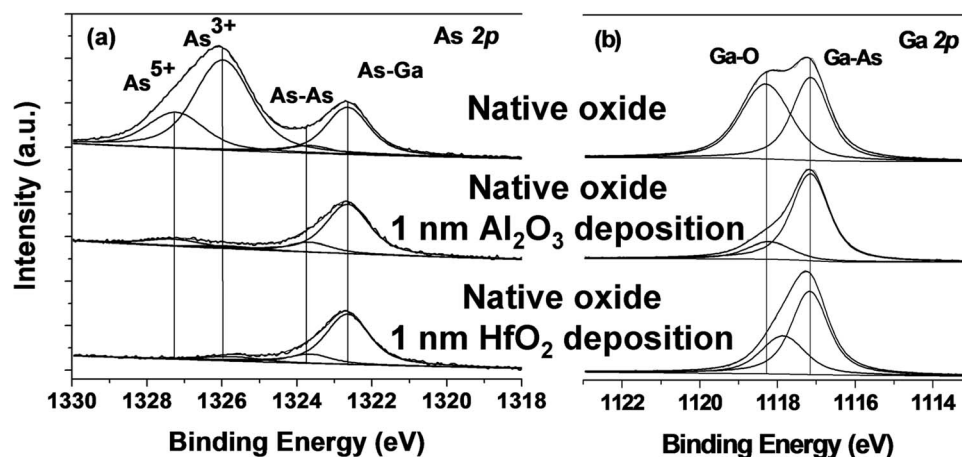


FIG. 1. (a) As  $2p_{3/2}$  and (b) Ga  $2p_{3/2}$  spectra showing oxidation state differences for a native oxide and subsequent 1 nm  $\text{Al}_2\text{O}_3$  and  $\text{HfO}_2$  depositions on a GaAs surface.

reduced, there is still Ga–O remaining at the interface after the ALD step and significantly more left behind than As–O. This is consistent with previous work by Kruse *et al.* regarding the selective reactivity of As–Ga backbonds with molecular  $\text{O}_2$ .<sup>14</sup> Both high- $k$  deposition processes remove more than 50% of the total Ga–O signal with the  $\text{Al}_2\text{O}_3$  deposition process removing slightly more. There is once again a difference in the oxide species that is attacked by the two separate precursors. The  $\text{HfO}_2$  deposition has resulted in a Ga–O peak that is centered at a lower binding energy than the resulting Ga–O feature post  $\text{Al}_2\text{O}_3$  deposition. This is consistent with the removal of the higher oxidation states (i.e.,  $\text{Ga}^{5+}$ ,  $\text{Ga}^{4+}$ ) by the TEMA-Hf precursor similar to the As–O removal. This binding energy shift could also be due to charge redistribution from second nearest neighbor changes in the Ga–O bonding environment. The self-cleaning effect is precursor and oxidation state dependent.

Figure 2(a) shows the As  $2p$  spectra for starting surfaces after degrease and  $\text{NH}_4\text{OH}$  surface treatment and the subsequent 1 nm  $\text{Al}_2\text{O}_3$  and  $\text{HfO}_2$  depositions. As reported previously,<sup>1,11</sup> the  $\text{NH}_4\text{OH}$  treatment removes the  $\text{As}^{5+}$  oxidation state and the As–O peak in this figure can be fully described by the  $\text{As}_2\text{O}_3$  feature. As described above, the TMA precursor removes this  $\text{As}^{3+}$  oxidation state leaving an interface that is free of As–O when the  $\text{NH}_4\text{OH}$  treatment is combined with the  $\text{Al}_2\text{O}_3$  deposition. The  $\text{HfO}_2$  deposition does not result in an As–O free surface due to the fact that the precursor does not completely remove the  $\text{As}^{3+}$  oxidation state that remains post  $\text{NH}_4\text{OH}$  treatment.

The Ga  $2p$  spectrum of Fig. 2(b) also shows the reduction in surface oxides after  $\text{NH}_4\text{OH}$  treatment and high- $k$  deposition. The total amount of Ga–O is reduced via  $\text{NH}_4\text{OH}$  treatment. Once again, the peak energy of the Ga–O feature appears at different binding energies after each of the two high- $k$  precursors are introduced. The  $\text{HfO}_2$  deposition results in the removal of higher Ga oxidation states leading to a lower binding energy feature with various possible Ga–O bonding configurations.

The reduction of the oxides during the ALD depositions may be expected based on the Gibbs free energies for forming  $\text{Al}_2\text{O}_3$  and  $\text{HfO}_2$  compared to As and Ga oxides.  $\text{Al}_2\text{O}_3$  and  $\text{HfO}_2$  formation is energetically preferred to the native oxides of GaAs, and the As oxides are less stable than the Ga oxides showing that bond energy is an important factor in the observed effect of more As–O bonding removal than Ga–O bonding.<sup>12,15</sup> It seems clear, however, that the (bond scission) reaction kinetics which are precursor specific play an important role in regard to the oxidation state reaction specificity.

We now speculate on the potential selective oxidation state reaction mechanisms. In the case of  $\text{Al}_2\text{O}_3$ , the Al is in a 3+ oxidation state which is consistent with the selective removal of the  $\text{As}^{3+}$  oxidation state. The Al atoms, bound to a trimethyl molecule could possibly replace the As atoms that are bound in an  $\text{As}_2\text{O}_3$  configuration through ligand exchange.<sup>6,16</sup> Other reaction pathways are possible including already oxidized Al interacting with the native oxides or a two step reaction occurring. The ligand exchange mechanism is not as favorable for the TMA molecule with the  $\text{As}_2\text{O}_3$

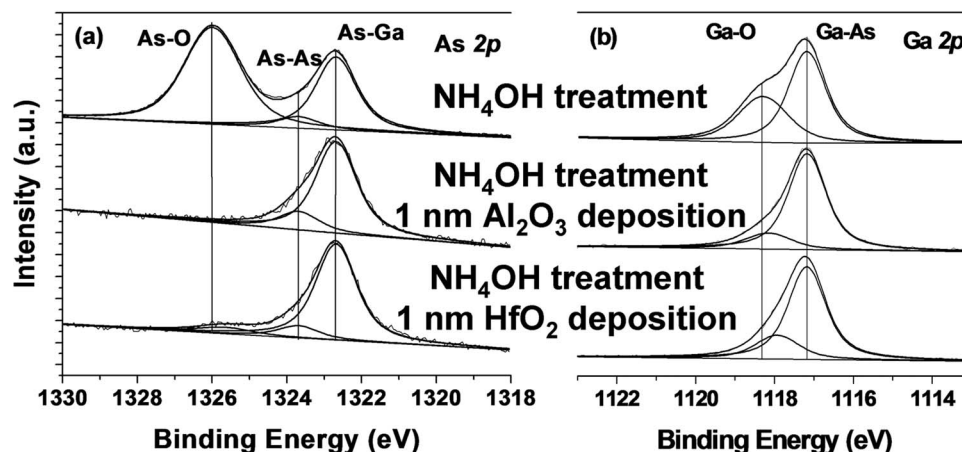


FIG. 2. (a) As  $2p_{3/2}$  and (b) Ga  $2p_{3/2}$  spectra showing oxidation state differences following  $\text{NH}_4\text{OH}$  surface treatment and subsequent 1 nm  $\text{Al}_2\text{O}_3$  and  $\text{HfO}_2$  depositions on a GaAs surface.

bonding arrangement. For  $\text{HfO}_2$ , the Hf is in a 4+ oxidation state which is not an exact complement of either As oxidation states. With no direct ligand exchange chemically favorable, the reduction of As oxidation states using TEMA-Hf must be due to other reasons.

The removal of  $\text{As}_2\text{O}_5$  before  $\text{As}_2\text{O}_3$  seems contradictory when compared with published equilibrium thermodynamic data for room temperature.<sup>12</sup> A possible explanation is the coordination of the Hf atom versus the As in the native oxide. The coordination of the Hf atom can be 6, 7, or 8 but remains in approximately a 4+ oxidation state regardless of coordination due to bond ionicity.<sup>17</sup> First-principles calculations have shown that higher oxygen coordination of the Hf in  $\text{HfO}_2$  is more stable than lower coordination Hf.<sup>18</sup> This suggests that despite the bulk thermodynamic values of As–O, it may be energetically favorable for the Hf to replace the higher coordinated As of  $\text{As}_2\text{O}_5$  rather than force the Hf into a lower coordination state to remove  $\text{As}_2\text{O}_3$ . There are also studies that propose  $\text{As}_2\text{O}_5$  is transformed into  $\text{As}_2\text{O}_3$  with excess  $\text{O}_2$  given off as a byproduct.<sup>19,20</sup> We also note that steric hindrance effects may be expected to play a significant role in the high-*k* deposition process not removing all of the native oxides as would be predicted based on equilibrium reactions. Studies are ongoing to interpret the reaction pathways in more detail for comparison to those observed on Si surfaces.<sup>21</sup> The “clean-up effect” using ALD, therefore, appears to be governed by simple charge balance, energy considerations due to oxygen coordination, and thermodynamics.

In summary, we have shown the reduction and in some cases the removal of As–O and Ga–O bonds on GaAs through high-*k* ALD deposition using TMA and TEMA-Hf as the metal precursors. This interfacial self-cleaning is shown to be precursor dependent as well as oxidation state dependent. Thermodynamics and compatibility of oxidation states explain the specific oxides that are removed and why some remain. These conclusions also suggest that interfacial bonding can be discriminately chosen with the proper selection of ALD precursor with particular attention paid to the oxygen coordination and valence charge state of the metal atom, and the Gibbs free energies of formation of its oxides.

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