

GaAs interfacial self-cleaning by atomic layer deposition

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The reduction and removal of surface oxides from GaAs substrates by atomic layer deposition (ALD) of Al₂O₃ and HfO₂ 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.¹ Previous *ex situ* studies of Al₂O₃ and HfO₂ 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 precursor² for Al₂O₃ as well as no interfacial oxide reduction using HfCl₄ as the precursor for HfO₂ ALD films³ at 300 °C. Dalapati *et al.* reported that some remnant oxides are detected after similar ALD processes at 300 °C.⁴ Huang *et al.*⁵ and Chang *et al.*⁶ have reported the removal of As oxides on InGaAs using Al₂O₃ (TMA) and HfO₂ [tetrakis (ethylmethylamino) hafnium (TEMA-Hf)], respectively. Shahrjerdi *et al.*⁷ 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 Al₂O₃ and HfO₂ 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% NH₄OH.⁸ *In situ* Al₂O₃ and HfO₂ thin films were deposited on GaAs in a Picosun ALD reactor integrated to a UHV multitechnique deposition/characterization system (base

pressure = 2×10^{-11} mbar) (Ref. 9) at a substrate temperature of 300 °C and a base pressure of ~ 700 mTorr. TMA and TEMA-Hf, delivered through heated lines/valves, were used as the metal organic precursors for Al₂O₃ and HfO₂ formation, respectively. The oxygen source was de-ionized H₂O. The metal organic was the first precursor pulse followed by the H₂O to complete one cycle (1 cycle ≈ 0.1 nm). Analysis of the deposited films was done using an *in situ* monochromatic XPS using an Al K α (1486.7 eV) x-ray source with a linewidth of ~ 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, As³⁺ and As⁵⁺, corresponding to As₂O₃ and As₂O₅, respectively.¹⁰ 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.^{10–12} After 1 nm Al₂O₃ deposition, the As oxide peak is greatly reduced and can be fit with only the As⁵⁺ oxidation state feature. Exposure to the TMA precursor with H₂O at 300 °C results in the reduction of the As³⁺ oxidation state intensity to below XPS detectable limits, consistent with previous reports.^{2,3,6} In contrast, after 1 nm HfO₂ deposition, the As⁵⁺ oxidation state intensity has been reduced, while a remnant As³⁺ 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 H₂O) which removes the native oxides and most of the reduction occurs during the first TMA pulse.¹³

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 Ga³⁺ and Ga⁵⁺ as well as other oxide species probably including Ga₂O, GaO₂, and Ga suboxides as well as GaAsO₄.¹² 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

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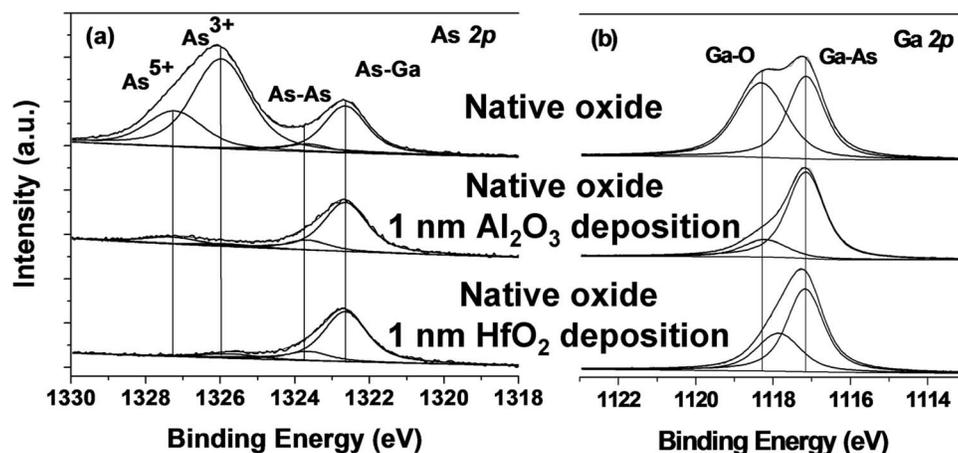


FIG. 1. (a) As $2p_{3/2}$ and (b) Ga $2p_{3/2}$ spectra showing oxidation state differences for a native oxide and subsequent 1 nm Al_2O_3 and HfO_2 depositions on a GaAs surface.

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 O_2 .¹⁴ Both high- k deposition processes remove more than 50% of the total Ga–O signal with the Al_2O_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 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 Al_2O_3 deposition. This is consistent with the removal of the higher oxidation states (i.e., Ga^{5+} , 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 NH_4OH surface treatment and the subsequent 1 nm Al_2O_3 and HfO_2 depositions. As reported previously,^{1,11} the NH_4OH treatment removes the As^{5+} oxidation state and the As–O peak in this figure can be fully described by the As_2O_3 feature. As described above, the TMA precursor removes this As^{3+} oxidation state leaving an interface that is free of As–O when the NH_4OH treatment is combined with the Al_2O_3 deposition. The HfO_2 deposition does not result in an As–O free surface due to the fact that the precursor does not completely remove the As^{3+} oxidation state that remains post NH_4OH treatment.

The Ga $2p$ spectrum of Fig. 2(b) also shows the reduction in surface oxides after NH_4OH treatment and high- k deposition. The total amount of Ga–O is reduced via NH_4OH 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 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 Al_2O_3 and HfO_2 compared to As and Ga oxides. Al_2O_3 and 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.^{12,15} 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 Al_2O_3 , the Al is in a 3+ oxidation state which is consistent with the selective removal of the As^{3+} oxidation state. The Al atoms, bound to a trimethyl molecule could possibly replace the As atoms that are bound in an As_2O_3 configuration through ligand exchange.^{6,16} 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 As_2O_3

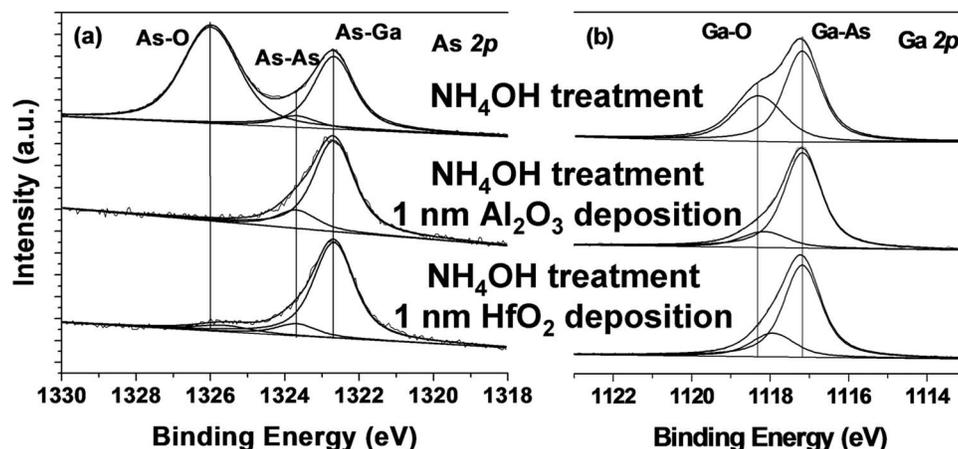


FIG. 2. (a) As $2p_{3/2}$ and (b) Ga $2p_{3/2}$ spectra showing oxidation state differences following NH_4OH surface treatment and subsequent 1 nm Al_2O_3 and HfO_2 depositions on a GaAs surface.

bonding arrangement. For 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 As_2O_5 before As_2O_3 seems contradictory when compared with published equilibrium thermodynamic data for room temperature.¹² 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.¹⁷ First-principles calculations have shown that higher oxygen coordination of the Hf in HfO_2 is more stable than lower coordination Hf.¹⁸ 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 As_2O_5 rather than force the Hf into a lower coordination state to remove As_2O_3 . There are also studies that propose As_2O_5 is transformed into As_2O_3 with excess O_2 given off as a byproduct.^{19,20} 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.²¹ 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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