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Investigation of interfacial oxidation control using sacrificial metallic Al and La passivation layers on InGaAs

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The ability of metallic Al and La interlayers to control the oxidation of InGaAs substrates is examined by monochromatic x-ray photoelectron spectroscopy (XPS) and compared to the interfacial chemistry of atomic layer deposition (ALD) of $\text{Al}_2\text{O}_3$ directly on InGaAs surfaces. Al and La layers were deposited by electron-beam and effusion cell evaporators, respectively, on $\text{In}_{0.53}\text{Ga}_{0.47}\text{As}$ samples with and without native oxides present. It was found that both metals are extremely efficient at scavenging oxygen from III–V native oxides, which are removed below XPS detection limits prior to ALD growth. However, metallic Ga/In/As species are simultaneously observed to form at the semiconductor–metal interface. Upon introduction of the samples to the ALD chamber, these metal bonds are seen to oxidize, leading to Ga/In–O bond growth that cannot be controlled by subsequent trimethyl-aluminum (TMA) exposures. Deposition on an oxide-free InGaAs surface results in both La and Al atoms displacing group III atoms near the surface of the semiconductor. The displaced substrate atoms tend to partially oxidize and leave both metallic and III–V oxide species trapped below the interlayers where they cannot be “cleaned-up” by TMA. For both Al and La layers the level of Ga–O bonding detected at the interface appears larger then that seen following ALD directly on a clean surface. © 2012 American Vacuum Society. [http://dx.doi.org/10.1116/1.4721276]

I. INTRODUCTION

Research on III–V substrates for the microelectronics industry has defined the quality of the insulator/substrate interface as arguably the greatest obstacle for widespread adaptation of this material system in future technology nodes. Without the use of an interface passivation layer (IPL), the defect density of this interface is such that the Fermi level becomes pinned and an anomalous frequency dispersion phenomenon in accumulation capacitance is observed. Recent work has revisited the use of thin IPLs for III–V metal-oxide-semiconductor (MOS) gate stacks with great success. Work by Oktyabrsky et al. and Zhu et al. has shown that parameters such as oxide and IPL thickness can be varied in order to optimize the performance of MOS capacitors utilizing Si-IPLs. The general hypothesis is that these layers inhibit the formation of surface oxides of Ga and As during device processing, which likely result in the formation of the defects leading to Fermi level pinning. For example, a recent study by Hinkle et al. demonstrated that the deleterious capacitance behavior is related to the formation of interfacial $\text{Ga}_2\text{O}_3$. Additionally it was shown that the $\text{Ga}^{1+}$ oxidation state of gallium ($\text{Ga}_2\text{O}$) does not appear to contribute to frequency dispersion. Unfortunately the use of an Si-IPL leads to the formation of a thin, relatively low-$k$ SiO$_2$ layer, which would put a limit on the attainable gate stack capacitance of devices based on this technology. With this in mind, the work presented here attempts to evaluate the use of metallic Al- and La-IPLs that, when oxidized, form high-$k$ oxides. This study is performed in situ, where with the use of monochromatic x-ray photoelectron spectroscopy (XPS), the obtained interfaces are evaluated for their overall chemical composition and behavior during subsequent atomic layer depositions (ALD) using an in situ “half-cycle” approach outlined in previous studies. The impact of the metallic layers, on both oxidized and oxide-free $\text{In}_{0.53}\text{Ga}_{0.47}\text{As}$ surfaces, is compared to the “clean-up effect” by trimethyl-aluminum (TMA) during ALD.

The formation of metal–GaAs interfaces has been extensively researched in terms of the generation of Ohmic contacts and Schottky barriers at the metal semiconductor interface, with Al, Cu, Ni, Ag, Ge, and Si getting particular attention. In the case of deposition of Al on GaAs, Al is seen to replace Ga (and for InGaAs the same is likely to be the case for the In also) in the subsurface layers forming AlAs, liberating the Ga and In to form metal states through the replacement reaction,
than that of SiO₂, it will still be desirable to have a material as well as the interaction with any excess As that forms during deposition through the following reaction:

$$\text{Al} + (\text{In})\text{GaAs} \rightarrow (\text{In})\text{Ga}_{1-x}\text{Al}_{x}\text{As} + x(\text{In})\text{Ga},$$  \hspace{1cm} (1)

as well as the interaction with any excess As that forms during deposition through the following reaction:

$$\text{Al} + (\text{In})\text{GaAs}_{1+y} \rightarrow \text{AlAs}_{x} + (\text{In})\text{GaAs}_{1+(y-x)},$$  \hspace{1cm} (2)

Second layer Ga sites are thermodynamically more favorable than top layer sites, and smaller net kinetic energy barriers than third and deeper layers. These interactions are metal dependent, and in the case of Au deposition, the Au is seen to interact preferentially with Ga, generating excess As.

What is not clear, however, is what happens upon subsequent oxidation of these layers and whether it is possible to remove the defects that are generated during the deposition process, and to what extent this process compares to when a thin native oxide layer is already present at the interface. If we assume that the IPL will scavenge any oxygen present at the interface (or present during exposure to further deposition processes), in the case of Al this will likely form Al₂O₃ at the interface. While Al₂O₃ has a higher k value than that of SiO₂, it will still be desirable to have a material with larger k value present at the interface. For this reason, lanthanum oxide has been proposed as a potential high-k material for integration into next generation semiconductor devices. However, unlike Al, the interaction between La metal and the (In)GaAs surface is not well known, with very little information available regarding the interfacial chemistry that takes place upon deposition. This is likely due to the very high reactivity of La, which necessitates the use of in situ deposition and characterization techniques.

The effect of metal deposition and subsequent ALD of Al₂O₃ is first compared to direct ALD Al₂O₃ on an oxide-free surface. Considering the first cycle of the ALD process involves the interaction of the TMA molecule with the InGaAs surface, this allows for a direct comparison between the effect of substrate–metal ion interactions and Al growth through interactions between the semiconductor surface (metal dep) and the metal ligands (ALD). Since ALD is a surface controlled deposition process, the interactions between the Al in the TMA and subsurface layers of the InGaAs substrate are unlikely to take place, reducing the potential for metallic Ga and In generation. The growth of Al on the surface is limited by the number of ligand interactions that take place; until the surface is saturated by TMA reaction products. Since the Al is chemisorbed at the surface it is also unlikely to propagate into the substrate, with any excess energy generated in the interaction transferring to the liberated reaction products. However, based on the previously reported clean-up effect, the possibility of improving the interface between the substrate and the oxide layer after IPL deposition presents a potential method for enhancing the effectiveness of the IPL layer.

II. EXPERIMENT

Metallic Al- and La-IPLs were deposited in situ from electron-beam and effusion sources, respectively, to a thickness of 1 nm, measured with a quartz crystal monitor. The behavior of the Al- and La-IPLs was explored on oxide-free In₀.₅₃Ga₀.₄₇As surfaces as well as on a sample that underwent a 3 min etch in NH₄OH to remove the native oxide that was present due to atmospheric exposure.

The In₀.₅₃Ga₀.₄₇As used in this study was grown lattice matched on InP obtained from IntelliEpi. The oxide-free surface is obtained from wafers that were initially protected by a 50 nm thick arsenic capping layer deposited following MBE growth of the In₀.₅₃Ga₀.₄₇As layer. This film prevents native oxides from forming during ex situ handling but can then be desorbed in ultrahigh vacuum (UHV) with a 30 min anneal at 430 °C. In order to study the ability of the metal IPLs to modify native oxides some samples were obtained without this As cap. They were initially degreased for 1 min in each of acetone, methanol, and isopropyl alcohol. The native oxides were partially removed using an NH₄OH dip for 3 min followed by a rinse in flowing de-ionized water for <10 s. Samples were then mounted and introduced into a UHV system in less than 10 min. A dual chamber ALD reactor integrated to a UHV multitechnique deposition/characterization system was used for this in situ study. TMA was used as the Al precursor for subsequent Al₂O₃ formation using a water deposition chemistry at 300 °C.

XPS was carried out using a monochromatic Al Kα x-ray source (hν = 1486.7 eV) with a linewidth of 0.25 eV, and a 125 mm seven channel hemispherical electron energy analyzer at a pass energy of 15 eV. This is contained in a dedicated analysis chamber maintained at a base pressure of <5 × 10⁻¹¹ mbar and connected through a UHV transfer tube to the in situ deposition chambers. XPS spectra were taken of the As 3d, Ga 3d/In 4d, Ga 2p₁/₂, In 3d₅/₄, O 1s, C 1s, Al 2p, La 3d, and La 4d core levels to ensure consistent information was attained from different core levels of the same element, where possible. XPS peak fitting was carried out using AANALYZER, with details of the peak fitting process described previously.

III. RESULTS AND DISCUSSION

A. Al deposition

Figure 1 shows the highly surface sensitive Ga 2p₁/₂, As 2p₁/₂, as well as the In 3d₅/₄ spectra from the oxide-free InGaAs sample. The indium region, due to the lower (higher) binding (kinetic) energy of the core level, is not as surface sensitive as either that of the gallium or the arsenic 2p spectra shown here; however, it is the most surface sensitive core level available using an Al Kα x-ray source. The In spectra are further complicated due to the asymmetric nature of the In 3d core level line shape, which broadens the spectra at the higher binding energy side of the peak. This can lead to complications in spectral interpretation as this is a region in which indium oxidation states would be expected to appear. In order to simulate this asymmetric peak line shape, an extra peak is linked to the In 3d peak when it is clear that there is no detectable indium oxide present, based on the O 1s core level spectra. This line shape is then maintained throughout the analysis unless it is clear that the natural line shape of the core level has changed and cannot be fitted.
accurately without changing the parameters of the extra component. Due to the thermodynamic stabilities of indium related compounds it is expected that their behavior mimics gallium closely and this is further monitored and cross referenced to ensure as accurate peak deconvolution as possible. Following desorption of the As capping layer, the surface shows evidence of only Ga–As–In bonds, and from Fig. 2 the O 1s core level signal is below the level of detection and is referred to herein as an “oxide-free” surface.

Prior to the first TMA exposure the sample is inserted into the ALD reactor for 30 min in order to determine the effect of temperature and any residual species in this chamber. This exposure to the ALD reactor at 300 °C maintained at ~9 mbar results in mainly Ga$^{1+}$ formation and minimal Ga$^{3+}$ states appearing in the Ga 2p spectra, located at 0.55 and 1.1 eV from the bulk peak, respectively. Simultaneously, a signal in the O 1s spectra is detected (Fig. 2). Additionally As–As bonding is detected upon reactor exposure and is expected to accompany any Ga–O bond formation due to breaking of Ga–As bonds. As shown previously, the first TMA pulse reduces Ga$^{3+}$ bonds below the level of detection while some Ga$^{1+}$ remains. This transfer of oxygen from the substrate oxides is illustrated in the O 1s region in Fig. 2 as the peak shifts to a higher binding energy, with the emergence of a peak component associated with Al–O formation (~531.2 eV). The As–As peak is also reduced, with the concurrent emergence of a lower binding energy “As−” peak, suggesting possible formation of As surface states (dangling bonds or dimers), or As–Al bonds. The interface appears chemically passivated as, following further TMA and water exposures, the chemical configuration of gallium atoms is not significantly affected. This behavior is reflected in the ratio of the fitted oxide peak components to the bulk peak area shown in Fig. 3.

Interestingly, the As–As bond concentration relative to the bulk As–Ga bond appears to increase as the Al$_2$O$_3$ film grows. A possible explanation for this behavior is offered by Huang et al., as they observed arsenic at the top of their

![Fig. 1](image1.png)
*Fig. 1. (Color online) Ga 2p$_{3/2}$, As 2p$_{3/2}$, and In 3d$_{5/2}$ core level spectra from a decapped InGaAs sample, following exposure to the ALD reactor chamber, and then after subsequent half-cycle ALD precursor exposures up to 1 nm of Al$_2$O$_3$. An extra feature is introduced in the In spectra to fit the asymmetry of the In line shape. See the text.*

![Fig. 2](image2.png)
*Fig. 2. (Color online) O 1s core level spectra from a decapped InGaAs sample following exposure to the ALD reactor chamber, and then after subsequent half-cycle ALD precursor exposures up to 1 nm of Al$_2$O$_3$.*

![Fig. 3](image3.png)
*Fig. 3. (Color online) Ratio of the fitted core level oxide to bulk peak components from the Ga 2p$_{3/2}$, As 2p$_{3/2}$, and In 3d$_{5/2}$ spectra.*
The emergence of a peak at Al–substrate bonds is also visible in the Al 2p spectra compared to Ga and As, indicating As–Al formation, although at lower levels compared to Ga. The formation of Al–substrate bonds is also visible in the Al 2p region shown in Fig. 5(a). Overall these observations are a symptom of a chemical disruption of the pristine III–V surface through interaction of the metal atoms with the substrate, which was not the case with the first ALD cycle, highlighting that the presence of ligand interactions during the ALD process results in very different behavior compared to that for the metal atom only.

Exposure to the ALD chamber ambient causes some Ga3+, Ga1+, and In oxidation states to appear and simultaneously the metallic Ga and In peaks to be diminished. As evident from Fig. 5(a), the Al-IPL is almost fully oxidized at this stage, likely causing the oxidation of the Ga and In at the interface with the substrate. These oxide states appear to be located below the Al-IPL as further exposures to TMA and water pulses do not produce large changes in the spectrum, as evidenced by the ratio of the oxides to the substrate peaks in Fig. 5(b). Unfortunately, as shown by Hinkle et al.,5 the presence of Ga3+ chemical states at the interface will likely result in undesirable electrical characteristics.

The ability of TMA to clean-up interfacial oxides is largely due to the inherently higher affinity for oxygen exhibited by Al as compared to Ga and As.32 This property is explored by depositing metallic Al on the InGaAs surface that was treated with NH4OH. The Ga 2p3/2/As 2p3/2 spectra in Fig. 6 show residual gallium and arsenic oxides as well as As–As commonly found following an NH4OH treatment.33 Remarkably, following the deposition of the Al-IPL, both As and Ga oxides are reduced below the level of detection of XPS while As–As bonding is also diminished. As discussed earlier, the O 1s peak following the TMA exposure represents a mixture of residual substrate oxides and the newly formed Al–O bonds at higher binding energy. However, following the deposition of the Al-IPL the O 1s peak in Fig. 7(a) shifts dramatically to the O–Al position. This is consistent with the complete reduction of substrate oxides seen in Fig. 6.

As per previous ALD studies, this again suggests that the clean-up effect, as a result of interaction of the native oxides with TMA, proceeds through a ligand exchange mechanism.

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**Fig. 4.** (Color online) Ga 2p3/2, As 2p3/2, and In 3d5/2 core level spectra from a decapped InGaAs sample and following subsequent 1 nm deposition of Al metal and half-cycle ALD of 1 nm of Al2O3.
whereby the valency of the dominant oxide for the incoming metal precursor dictates which native oxide states will be removed.\textsuperscript{34,35} The removal of the native oxides upon the deposition of metallic Al is not restricted to relying on surface chemical interactions through ligand exchanges to allow interaction with the oxide, and as such is likely to be solely dependent on the magnitude of the formation energies for the individual states. The Gibbs free energy for Al\textsubscript{2}O\textsubscript{3} is reported to be significantly lower than that of any of the native oxide states present on the InGaAs surface and as such would be the most energetically favorable system.\textsuperscript{1,32}

Another significant difference to the TMA clean-up effect is that these Al-IPL experiments produce a detectable reduction product of the native oxides; metalliclike states. Therefore, in the presence of a native oxide on the surface the Al-IPL will reduce these rather than attacking the substrate as follows:

\[
(Ga/In/As)_2O_3 + 2Al \rightarrow Al_2O_3 + 2(Ga/In/As).
\]

This is contrary to the clean-up with TMA on the III–V surface, which produces no detectable reduction products and cannot completely remove Ga–O bonding. This further suggests that the species produced by TMA interactions are indeed volatile, as proposed elsewhere.\textsuperscript{7–9} Despite its inability to fully reduce native oxide bonds, and specifically Ga\textsubscript{2}O, with the trivalent TMA molecule mostly targeting the trivalent oxide states through a ligand exchange mechanism, the volatilization of the reduced gallium species is likely critical to the abrupt interfaces produced with ALD on III–V surfaces.\textsuperscript{36}

The suggestion is then that Al-IPL is indeed a poor chemical passivant, as highly reactive metallic species are left at the interface that immediately oxidizes inside the ALD reactor, although some Al–substrate bonds are seen to persist throughout, as indicated by the Al 2p spectra in Fig. 7(b). Looking at the ratio of the oxide components to the substrate peaks in Fig. 7(c) indicates that the level of Ga–O bonding does not change as a result of exposure of the sample to TMA, whereas the As and In–O ratios are seen to decrease to within detection limits with successive cycles. This suggests that the Ga–O persists at the interface between the Al–O and the substrate, preventing oxide clean-up from taking place.

![Figure 5](image_url)  
**Fig. 5.** (a). (Color online) Al 2p core level spectra from a decapped InGaAs sample and following subsequent 1 nm deposition of Al metal and half-cycle ALD of 1 nm of Al\textsubscript{2}O\textsubscript{3} and (b) the ratio of the fitted oxide to bulk peak components from the Ga 2p\textsubscript{3/2}, As 2p\textsubscript{3/2}, and In 3d\textsubscript{5/2} spectra.

![Figure 6](image_url)  
**Fig. 6.** (Color online) Ga 2p\textsubscript{3/2}, As 2p\textsubscript{3/2}, and In 3d\textsubscript{5/2} core level spectra from a decapped InGaAs sample and after subsequent \textit{ex situ} NH\textsubscript{4}OH treatment, 1 nm of Al deposition half-cycle up to 1 nm of ALD Al\textsubscript{2}O\textsubscript{3}.
B. La deposition

Recently, lanthanum oxides have been explored as possible high-$k$ materials on III–V surfaces due to the compatible chemistry as a group III element and its role in work function tuning.\textsuperscript{37–43} In addition to these factors, La—as an extremely electropositive element—allows the discernment of chemical states such as As–Ga\textsubscript{=As–Al} bonds from that of As–La. Up to this point, there has been very little work on the effect of depositing La metal directly onto the (In)GaAs surface and as such there is virtually no information regarding the expected interactions between the La and the substrate. With that in mind the interaction of the La-IPL with an oxide-free InGaAs surface is shown in Fig. 8. Initial observations of the Ga and As 2$p_{3/2}$ regions might indicate that the La-IPL behaves similarly to the Al-IPL; however, there are some significant differences. The deposition of La results in the formation of lower binding energy Ga and In peaks in their respective plots. The binding energy of these peaks is similar to that seen with the Al-IPL layer and, considering the significant difference in electronegativity between Al and La, this suggests that these peaks are due to metalliclike Ga–Ga and In–In bonding; however, some La bonding cannot be ruled out. In the case of the As peak, however, the emergence of a large lower binding energy peak, $\sim$0.75 eV from the bulk peak, is clearly detected, indicating significant levels of As–La bonding taking place. This is in contrast to the Al-IPL case, where As–Al bonding was at a very low level. There is also no evidence of As–As formation taking place.

If we contrast this to the case of LaAlO$_x$ deposition by ALD on the atomically clean In$_{0.2}$Ga$_{0.8}$As case carried out by Aguirre-Tostado \textit{et al.},\textsuperscript{43} where the La precursor was used as the first cycle in the deposition process and as such is a good allegory to the La metal deposition here, there is no evidence of Ga–Ga or In–In formation taking place in the Ga 2$p$ and In 3$d$ spectra. Also, for the As 2$p$ spectra, there is no evidence of the large lower binding energy peak seen in this study, although As–As bond formation is detected due to disruption of the In$_{0.2}$Ga$_{0.8}$As surface. This all highlights the significantly reduced interaction of the ALD La with the InGaAs substrate in comparison to direct metal deposition, due to the ligand interactions, which localize the La growth at the semiconductor surface.

Exposure to the ALD chamber at 300 °C causes gallium, indium, and arsenic oxidation, as well as emergence of large amounts of As–As bonding. This is concurrent with oxidation of the La layer, with the La 3$d$ spectra in Fig. 9(a) having a peak position indicative of La$_2$O$_3$ or La(OH)$_3$. This is further confirmed by looking at the separation between the core level orbital peak and the peak due to the final state effect as a result of the bonding component of charge transfer from the ligand valence band to the core level ($\sim$4 eV), as well as the total spectral peak shape. This all suggests that the La–O is primarily in the form of La(OH)$_3$.\textsuperscript{44} Determining the exact nature of the oxide layer from the O 1$s$ layer in Fig. 9(b) is difficult due to the number of spectral components needed to accurately deconvolute the spectra, making accurate assignment more complex; however, the presence of components at the higher binding energy side of the spectra are again indicative of hydroxide formation.

After the anneal, metallic Ga or In is no longer detected, with the As–La state also greatly reduced. The Ga–O and In–O states formed as a result of exposure to the ALD reactor are not affected following TMA/water exposures, highlighted by the ratio of the oxide components to the corresponding substrate peaks in Fig. 9(c), suggesting that, again, these are located at the interface between the La–O and the substrate with the TMA unable to interact with it.
Interestingly, the As$^{3+}$ states are reduced by the subsequent TMA exposure, indicating that they may have formed on top of the La layer; however, it is also possible that arsenic oxides will reduce over time due to the elevated temperatures in the ALD reactor, potentially with oxygen transfer to gallium and indium,\textsuperscript{23} or to the La layer.

From the Al 2$p$ spectra in Fig. 9(d), it appears that with the first few cycles of TMA and water, based on the binding
energy position of the peak, there appears to be interaction between the La–O layer and the TMA. This manifests itself as a peak at a lower binding energy than would be expected for Al₂O₃, again consistent with La having a much lower electronegativity than Al. With subsequent cycles up to 1 nm of Al₂O₃ growth, we see the peak shift to a higher binding energy, suggesting more uniform Al₂O₃ formation; however, it is possible that Al–La–O bonding persists at the interface between the Al₂O₃ and the La-IPL.

IV. SUMMARY AND CONCLUSIONS

This study has revealed that on a pristine oxide-free surface, Al- and La-IPLs disrupt the system by breaking III–V bonds. In general, the ALD reactor environment oxidizes the metal layers and leads to Ga-O bond regrowth that cannot be controlled by subsequent TMA exposures. Unlike TMA clean-up, the La/Al-IPLs generate reduction products in the form of metallic Ga and In states, which in the case of the Al-IPL are not removed upon oxidation of the Al. This observation supports earlier claims that reduction products of gallium oxides are volatilized during ALD. This metal interaction is mediated in the case of ALD due to the interaction of the precursor ligands with the substrate ensuring a surface localized growth and preventing the formation of group III metallic states.

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