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<td>Milojevic, M.; Contreras-Guerrero, Rocio; O'Connor, Éamon; Brennan, B.; Hurley, Paul K.; Kim, J.; Hinkle, C. L.; Wallace, Robert M.</td>
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In-situ characterization of Ga$_2$O passivation of In$_{0.53}$Ga$_{0.47}$As prior to high-k dielectric atomic layer deposition


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**In-situ** characterization of Ga$_2$O passivation of In$_{0.53}$Ga$_{0.47}$As prior to high-k dielectric atomic layer deposition

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Ga$_2$O interfacial passivation layers (IPLs) on In$_{0.53}$Ga$_{0.47}$As are investigated using in-situ monochromatic x-ray photoelectron spectroscopy. The oxide is entirely composed of Ga$_2$O when deposited with an effusion cell temperature of 1500°C and substrate temperature of 425°C. The growth on In$_{0.53}$Ga$_{0.47}$As reveals slight chemical modification of the surface. The Ga$_2$O behavior and ability to protect the III-V surface are observed following Al$_2$O$_3$ deposition by atomic layer deposition following each precursor pulse. Al$_2$O$_3$ growth by trimethyl-Al (TMA) and water reveals that the IPL undergoes the “clean-up” effect following TMA exposures causing As-As bonding formation resulting in a high interface state density. © 2011 American Institute of Physics.

Research on III-V substrates for metal oxide semiconductor field effect transistor (MOSFET) applications has focused on improving the quality of the insulator/substrate interface since it represents a major obstacle for widespread adaptation of this material system in future technology nodes. The defect (trap) density ($D_T$) of this interface can be quite high, pinning the Fermi level and resulting in significantly degraded transport properties. Recent theoretical studies$^{2,3}$ and previous experimental work$^4$ indicate that the suppression of particular interfacial oxidation states can reduce this $D_T$ and improve the performance of III-V based materials. Strategies such as Si (Refs. 5 and 6) and Ge (Ref. 7) interfacial passivation layers (IPLs) and Gd containing materials. Strategies such as Si (Refs. 5 and 6) and Ge (Ref. 7) interfacial passivation layers (IPLs) and Gd containing interfacial oxides$^8$–$^{10}$ have been employed in an attempt to control the chemical species present at the interface. Previous work has indicated the presence of Ga$_2$O at the interface of devices showing improved capacitance-voltage (CV) and drain current-gate voltage ($I_d$–$V_g$) characteristics on GaAs(100). Additionally, first principles calculations$^{2,11}$ as well as scanning tunneling microscopy reports$^{16}$ indicate that Ga$_2$O-like interfacial bonding on GaAs(100) does not result in gap states. Previous reports of molecular beam epitaxy (MBE) grown GGO on InGaAs have reported the inclusion of a Ga$_2$O “template layer”$^{12}$ that deposits initially on the InGaAs surface before the full stoichiometric GGO is formed. $D_T$ extraction from CV and conductance data indicate an improved interface, at least in terms of midgap $D_T$ levels.$^{12,14}$ However, in each of those studies, the MBE deposited dielectric thickness is on the order of 6 to 10 nm or more, precluding their use in scaled devices. In this work, thin (~0.3 nm) MBE deposited Ga$_2$O is investigated as a passivation layer prior to high-k atomic layer deposition (ALD) in an attempt to protect the bulk InGaAs from further oxidation and the formation of deleterious Ga dangling bonds and As-As bonds. The ALD conditions included trimethyl-Al (TMA) and H$_2$O pulse times of 0.1 s, N$_2$ purge times of 4 s, and gas flow rates of 200 sccm each. The substrate temperature was maintained at 300°C throughout the ALD process.

Ga$_2$O was grown from a high temperature effusion source from polycrystalline Ga$_2$O$_3$ contained in a custom iridium crucible. The evaporation of polycrystalline Ga$_2$O$_3$ at high temperatures is expected to result in Ga$_2$O deposition$^{15,16}$ since bulk Ga$_2$O$_3$ decomposes to form Ga$_2$O and O$_2$. Fortuitously, the sticking coefficient of Ga$_2$O on GaAs is six orders of magnitude larger than that of O$_2$ which should result in pure Ga$_2$O growth.$^{17}$

The Ga$_2$O is grown on 300 nm thick 1 $\times$ 10$^{17}$/cm$^3$ p-type doped In$_{0.53}$Ga$_{0.47}$As (100) on a 1 $\times$ 10$^{19}$/cm$^3$ p-type doped InP substrate following the in-situ thermal desorption of a protective 50 nm thick As-capping layer. Due to the ~450°C decapping temperature, electron diffraction (not shown) indicates a mixed (2 $\times$ 4)/(4 $\times$ 2) surface reconstruction as noted previously by Shen et al.$^{18}$ and serves as a control sample to establish the monochromatic x-ray photoelectron (XPS) spectra shape on the atomically clean surface that may be utilized for the careful spectral deconvolution performed here.$^{4,19}$ The Ga$_2$O films were deposited at 1350°C–1700°C effusion cell temperatures ($T_{\text{source}}$), while the substrate temperature was either room temperature or 425°C. The effect of effusion cell and substrate temperature on the chemical composition of the Ga$_2$O IPL is shown in Fig. 1 through the surface sensitive$^{20}$ Ga 2$p_3/2$ spectra. Following a 2 min deposition at $T_{\text{source}}$ = 1350°C onto a room temperature substrate, a convoluted spectrum (Fig. 1(a)) with the expected bulk substrate bonding, the Ga$_2$O (Ga$^{3+}$) bonding,$^4$ metallic gallium (Ga$^+$, e.g., Ga-Ga bonding) and Ga$_2$O$_3$ (Ga$^{3+}$) bonding is detected. This indicates that at lower $T_{\text{source}}$, the molecular beam chemistry is not simply Ga$_2$O and O$_2$ but possibly contains metallic Ga which then reacts with the O$_2$ also liberated by the source to form the additional states. If the deposition is performed with the same $T_{\text{source}}$ = 1350°C and the elevated substrate temperature $T_{\text{sub}}$ = 425°C, only the bulk Ga-As state remains.

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However, if the effusion cell temperature is raised to $T_{\text{source}} = 1500 \, ^\circ\text{C}$ (deposition rate $\sim 0.1 \, \text{nm/min}$), only Ga$^{1+}$ bonding is detected in addition to the bulk Ga-As (Fig. 1(b)) indicating that Ga$_2$O is the deposited species coming from the molecular beam. It should be noted that depositions were also performed at $T_{\text{source}} < 1300 \, ^\circ\text{C}$ and as high as 1700 $^\circ\text{C}$ (not shown). The low temperature ranges resulted in no detectable depositions while the higher temperatures resulted in overly rapid deposition rates. Hence, the optimal deposition conditions for thin IPLs were chosen ($T_{\text{source}} = 1500 \, ^\circ\text{C}$, $T_{\text{sub}} = 425 \, ^\circ\text{C}$). For the half-cycle studies and the correlated device fabrication, a 0.3 nm Ga$_2$O interface passivation layer was deposited.

As suggested previously, the deposition of Ga$_2$O on InGaAs and GaAs would ideally result in Ga$_2$O units bonding to the As at the surface or on row edges. This surface reaction should be difficult to detect using XPS with the As spectrum as this would manifest as As-Ga bonding at a nearly identical binding energy as that of the bulk As-Ga from the substrate. The As 2$p_{3/2}$ spectra in Fig. 1(c), however, displays a broadening of the peak as compared to the spectrum of a decapped pristine bulk substrate and is attributed to the slight disruption of the surface As following Ga$_2$O deposition creating an increased level of As-Ga bond disorder. This can be thought of as two convoluted As-Ga signals, one arising from the bulk pristine crystal surface and the other from the Ga$_2$O attachment to the surface As. The spectrum is therefore shown with two peaks having similar binding energies but different Gaussian widths.

It is noted that there is no As-O detected following these depositions or the subsequent ALD Al$_2$O$_3$ described later. Additionally, the In 3$d_{5/2}$ spectrum displays a change in the peak profile following Ga$_2$O deposition (not shown). This change occurs on the high binding energy side of the bulk peak and may include the oxidation of In. However, due to the difficulty in deconvoluting the In spectrum due to inherent asymmetries, the root cause of this surface alteration requires further study.

In order to evaluate the stability of the Ga$_2$O IPL during ALD depositions, the As 2$p_{3/2}$ and Ga 2$p_{3/2}$ spectra for an In$_{0.53}$Ga$_{0.47}$As sample are shown in Fig. 2(a) following each individual TMA and H$_2$O precursor pulses as well as following the deposition of a 1 nm Al$_2$O$_3$ film using methods described previously. 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 (base pressure $\sim 10^{-3}$ mbar). These spectra are identical to the spectra before the ALD exposure indicating that the Ga$_2$O layer is stable in the ALD reactor environment prior to precursor exposure.

Exposure to TMA results in a slight reduction of the Ga$_2$O intensity as has been shown previously with (non-MBE) native Ga-oxides via the cleanup effect. In addition, there is the emergence of As-As (As$^0$) bonding as well which may be responsible for mid-gap D$_{it}$. Exposure to the first water pulse does not change the chemical configuration as both the As and Ga regions are identical to the previous spectra. Unlike similar experiments on III-V oxides that show completed reactions following the first TMA pulse, this Ga$_2$O IPL undergoes a second reduction following further TMA exposures and even some Ga$_2$O regrowth following water pulses up to the final 1 nm Al$_2$O$_3$ ALD film. There is no interfacial Ga$_2$O$_3$ detected in these experiments which is one of the requirements to reduce interfacial traps. However, with each cycle,
the as-As bond concentration continues to increase (Fig. 2(b)) indicating that the Ga$_2$O IPL is ineffective at preventing the gradual formation of this chemical state during ALD growth. It is noted, however, that the initial formation of such bonding is near the detection limit, in contrast to prior studies without such MBE Ga$_2$O interfacial layers present where chemical preparations were employed.\(^{23,24}\)

To investigate the electrical characteristics of these interfaces, MOS capacitors were fabricated on identical In$_{0.53}$Ga$_{0.47}$As substrates. The capacitor dielectric stack consisted of the Ga$_2$O IPL followed by 8 nm of Al$_2$O$_3$ with a gate metal of Ni/Au. As can be seen in the C-V characteristics (Fig. 3), there is a significant amount of frequency dispersion over the entire bias range examined, indicative of high Dit and Fermi level pinning. If we assume that the As-As antisite density\(^{25,26}\) is below the limit of detection in the near surface region sampled by XPS, we speculate that this Dit is related to the As-As dimer bonding that arises during exposure to the ALD deposition and may prevent Ga$_2$O from being an effective passivation layer for such III-V channel materials under these conditions.

The results demonstrate that growth of pure Ga$_2$O layers from polycrystalline Ga$_2$O$_3$ occurs at a $T_{\text{source}}$ of 1500°C and a $T_{\text{sub}}$ of 425°C. The grown IPL is stable under standard ALD reactor conditions and hence possibly appropriate for subsequent \textit{ex-situ} fabrication as well. However, this Ga$_2$O IPL is not impervious to modifications by TMA and water exposure during the high-$k$ atomic layer deposition. Under these conditions, the IPL gets significantly reduced and results in the formation of interfacial As-As bonding, high Dit, and poor C-V characteristics.

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