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In situ surface pre-treatment study of GaAs and $In_{0.53}Ga_{0.47}As$

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The impact of using multiple cycles of trimethyl-aluminum (TMA) prior to Al_2O_3 deposition on the properties of $(NH_4)_2S$ treated $In_{0.53}Ga_{0.47}As$ and GaAs substrates was investigated by *in situ* x-ray photoelectron spectroscopy. Increasing the number of TMA cycles prior to Al_2O_3 atomic layer deposition (ALD) was seen to decrease the concentration of As-As detected at the oxide-semiconductor interface. The impact of annealing the $(NH_4)_2S$ treated GaAs surface *in situ* prior to ALD, in various environments, was also investigated. © *2012 American Institute of Physics*. [http://dx.doi.org/10.1063/1.3702885]

In order to keep up with scaling requirements of the semiconductor industry, the implementation of high mobility channels in metal oxide field effect transistors (MOSFETs) is expected to be necessary by future generations of semiconductor devices.[1] However, one of the major challenges in realizing this is engineering the interface between the channel material and the gate oxide.[2,3] The principal channel materials under investigation at the moment for n-type devices are arsenide based III-V materials, due to their high electron mobility, which is seen to scale with increasing indium content.[1] The native oxides of these materials have been shown to have poor electrical performance and so it is necessary to incorporate alternative high permittivity (high-k) oxide materials. Oxygen interaction at this interface has been predicted and shown to generate defects in the form of As-As bonding (e.g., dimers) and Ga dangling bonds at this interface.[4,5] As a result, methods to passivate the III-V surface have been utilized in order to reduce the oxygen interaction and prevent defects from being generated, prior and during high-k oxide growth.[6–9] However, high interfacial defect densities (D_{it}) are still seen with the majority of these processes, and as such significant refinement of surface preparation procedures is still needed.[10] Recent studies have shown improved device characteristics by incorporating multiple cycles of trimethyl-aluminum (TMA) prior to atomic layer deposition (ALD) (Refs. 11 and 12); however, the justification for this has not been thoroughly explored.

This study investigates the effect of varying the number of trimethyl-aluminum pretreatment cycles prior to ALD of Al_2O_3, using *in situ* x-ray photoelectron spectroscopy (XPS) to determine what changes are taking place at the GaAs and $In_{0.53}Ga_{0.47}As$ surfaces. The impact of annealing the surfaces in different conditions prior to ALD is also explored.

The wafers used in this study were n-type $In_{0.53}Ga_{0.47}As$ (S doped 4×10^{17}) and GaAs (Si doped 2×10^{18}) and were initially degreased for 1 min each in acetone, methanol, and isopropanol followed immediately by an optimized ammonium sulfide treatment in 10% $(NH_4)_2S$ for 20 min at room temperature.[7] Such optimized sulphide treatments have recently been correlated with improved capacitor[8] and transistor[13] characteristics. The samples were then rinsed in flowing deionized water for 10 s. The InGaAs and GaAs samples were then cleaved in two, with one piece of each material mounted as "companions" onto two separate sample holders (i.e., each holder with one InGaAs and one GaAs sample companion set). These sample sets were then loaded into an ultra-high vacuum (UHV) deposition and analysis tool, described elsewhere,[14] within 7 min of removal from the $(NH_4)_2S$ solution.

One sample set would undergo a *single* pulse of TMA (0.1 s pulse time in 200 sccm of N_2 carrier gas) prior to Al_2O_3 deposition, while the other would receive *ten* pulses of TMA. XPS scans of the As $2p_{3/2}$, Ga $2p_{3/2}$, O $1s$, In $3d_{5/2}$, C $1s$, As $3d$, In $4d$, and Ga $3d$ core levels were taken, after initially loading the samples to UHV, upon exposure to the ALD reactor for 30 min at 300 °C (to replicate the conditions experienced by the samples during ALD), after TMA-only pre-treatments, and after 10 full cycles (TMA + H_2O) of Al_2O_3 deposition.

A third set of GaAs samples underwent the same $(NH_4)_2S$ chemical treatment, loaded into the UHV system and, subsequently, annealed in either UHV ($<1 \times 10^{-8}$ mbar), N_2 (10 mbar), or forming gas (10 mbar with 10% H_2) at 500 °C for 30 min, again without exposing the samples to atmosphere. XPS scans were taken before and after annealing. XPS was carried out using a monochromated Al Kα x-ray source ($h\nu = 1486.7$ eV) which is connected *in situ* to the ALD reactor though an UHV transfer tube maintained at a pressure of $<5 \times 10^{-10}$ mbar. XPS peak fitting was carried out using AANALYZER software,[15] with the detailed fitting procedure described elsewhere.[16] The ALD was carried out in a commercial Picosun ALD reactor, at a pressure of ~9 mbar, with TMA and H_2O pulse times of 0.1 s and high purity N_2 purge time of 4s.

The As $2p_{3/2}$ spectra from the GaAs and InGaAs samples, after exposure to the ALD reactor at 300 °C and with either one cycle or ten cycles of TMA, are shown in Figure 1. The $(NH_4)_2S$ treatment was seen to significantly decrease the concentration of arsenic oxides present on the surface when compared to a native oxide sample—with only trace amounts of As_2O_5, As_2O_3, and a sub oxide—labeled As 1+ and attributed to As_2O, detected on all samples. Upon introduction to the ALD reactor at 300 °C, As_2O_5 was reduced below the

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detection limit and the concentration of As_2O_3 was seen to significantly decrease. Upon exposure to the TMA pre-treatments, the As_2O_3 peak was decreased to within XPS detection limits on all four samples, confirming previous results which showed that the first cycle of the ALD deposition process was able to fully remove the As_2O_3 from the GaAs and InGaAs surfaces.[17,18] A small residual As 1+ peak was seen to persist even after the TMA pretreatments, which could be further evidence of the ligand exchange mechanism between the trivalent TMA molecule and As_2O_3 to form Al_2O_3 being the preferable reaction mechanism.[19] The As_2O state has also previously been reported to be thermally very stable in comparison to other As oxidation states, when it was present at the InGaAs surface.[16]

However, a peak attributed to As-As bonding was also seen to persist after TMA pretreatments and at an elevated level on the GaAs samples in comparison to the InGaAs samples, as seen in the ratio of the peak areas of the peaks to that of the bulk peaks (Figure 2). This difference in concentration could be due to increased reactivity of the GaAs surface, reflected in an initially higher level of oxide present after $(NH_4)_2S$ treatment in comparison to the InGaAs surface, based on the peak area of the O 1*s* spectra (not shown). Previous studies have proposed that these As-As bonds form as a result of the oxidation of the surface, principally forming gallium oxides due to Ga having a higher affinity for oxygen, leaving the interface locally arsenic rich and generating As-As anti-bonding sites.[5] The higher gallium concentration in GaAs compared to InGaAs could then also explain the increased As-As concentration seen here on the GaAs sample.

A variation in the concentration of As-As present when either one cycle or ten cycles of TMA are employed in pretreating the surface was also detected. With ten cycles of TMA, there is an overall decrease in As-As concentration relative to that observed after one cycle of TMA. However, there is also a concomitant emergence of a lower binding energy peak, labeled "As−" in the spectra, detected at an increased concentration with 10 cycles of TMA cycles and at a similar level on both GaAs and InGaAs. This component has been previously detected in synchrotron-based photoelectron emission studies.[20] It is possible that this is an indication of breaking of an As-As dimer at the surface, creating an arsenic dangling bond,[21] or also possibly As-Al bond formation.[22]

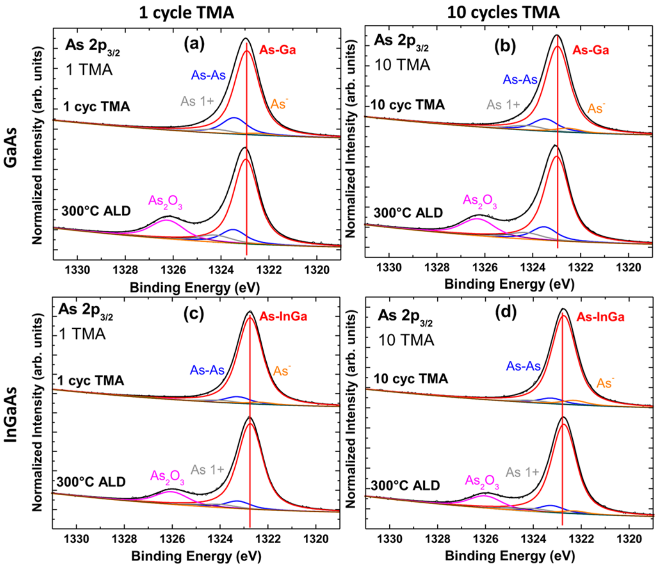

FIG. 1. XPS core level spectra for the As $2p_{3/2}$ peaks from GaAs [(a) and (b)] and $In_{0.53}Ga_{0.47}As$ [(c) and (d)] after exposure to the ALD reactor at 300 °C for 30 min, and with 1 cycle [(a) and (c)] or 10 cycles [(b) and (d)] of trimethyl-aluminum.

The corresponding Ga $2p_{3/2}$ and In $3d_{5/2}$ spectra from the GaAs and InGaAs samples, after introduction to the ALD reactor at 300 °C and after TMA pre-treatments, are shown in Figure 3. Upon annealing in the reactor, the gallium and indium oxides were seen to increase, due to an oxygen transfer from the reducing arsenic oxides.[16] The total oxygen concentration from the O 1*s* spectra was seen to decrease upon annealing, possibly due to the removal of some of these arsenic oxide species from the samples, as well as hydroxide related species. Upon TMA pre-treatment, the signal from the Ga_2O_3 is decreased to within detection limits of XPS, as well as a decrease in the concentration of the Ga 1+ state, without full removal.[6] This Ga 1+ (In 1+) state is likely due to a combination of Ga_2O (In_2O) and Ga-S (In-S) states that persist throughout the treatments here, with similar levels of sulfur detected on all four samples, based on the peak area of the S 2*p* peak (not shown). Sulfur is expected to preferentially bond with the group three elements.[23] The In $3d_{5/2}$ spectra in Figures 3(e) and 3(f) follow a similar trend to that of the Ga peaks, with no significant

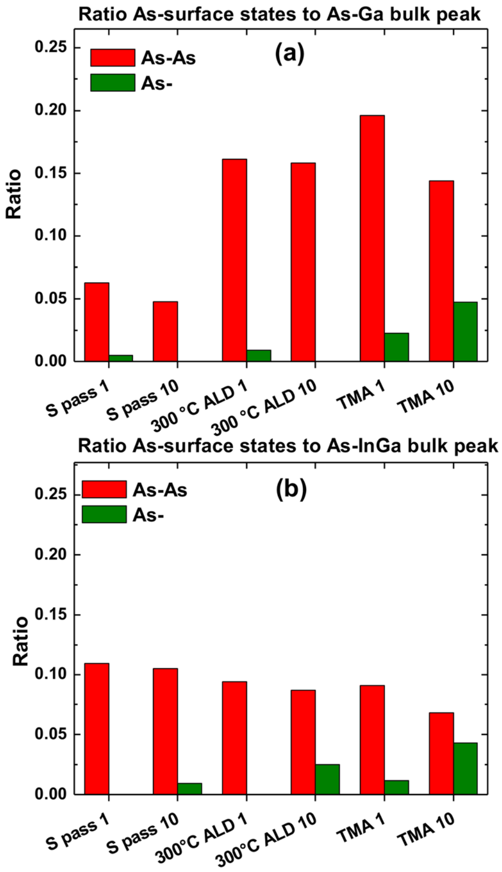

FIG. 2. Ratio of the fitted area of the As-As and As- components from the As $2p_{3/2}$ spectra for the GaAs (a) and $In_{0.53}Ga_{0.47}As$ (b) samples at different stages during sample processing, showing a decrease in the As-As peak area with increased number of TMA cycles.

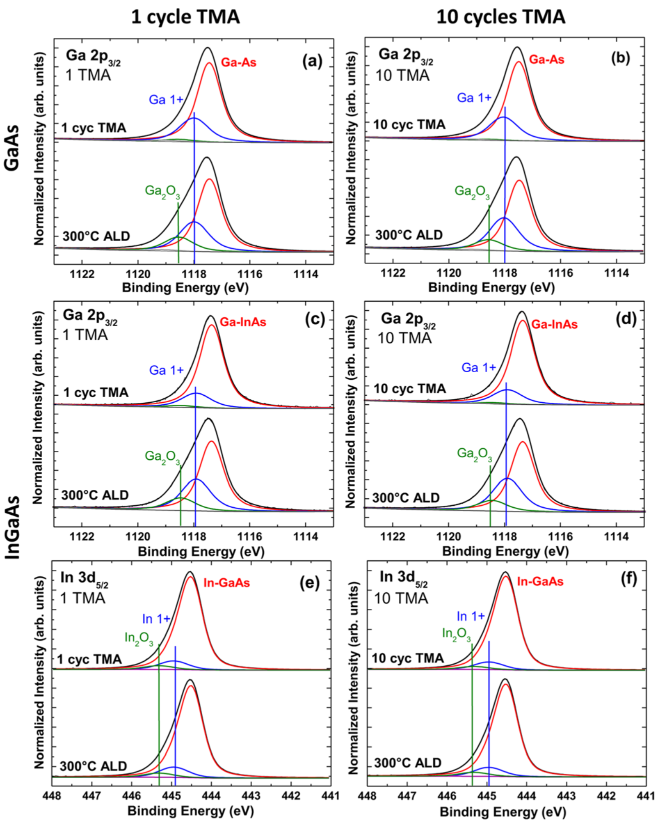

FIG. 3. Ga $2p_{3/2}$ (a)-(d) and In $3d_{5/2}$ (e) and (f) core level spectra from the GaAs and InGaAs samples after exposure to the ALD reactor at 300 °C for 30 min and after either one cycle [(a), (c), and (e)] or ten cycles [(b), (d), and (f)] of TMA.

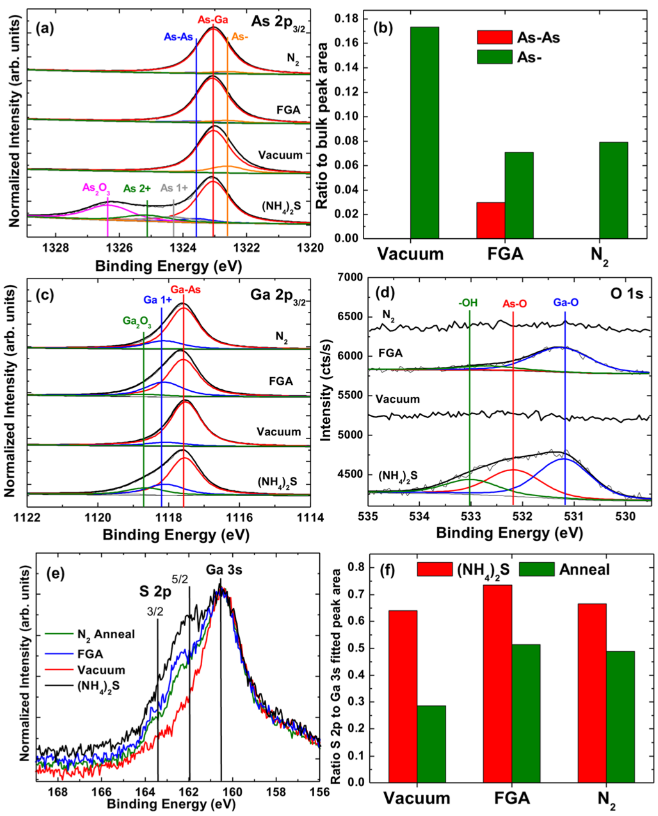

FIG. 4. XPS spectra after $(NH_4)_2S$ treatment of GaAs and subsequent anneals in UHV, forming gas, and N_2, from the (a) As $2p$, (c) Ga $2p$, (d) O $1s$, and (e) S $2p$ core levels. The ratios of the fitted As-As and As-features to the As $2p$ bulk peak area are shown in (b), and (d) shows the S $2p$ to Ga $3s$ fitted peak area ratio.

changes taking place with increased number of TMA cycles. Fitting of the In $3d_{5/2}$ peak is complicated by an apparent asymmetric lineshape for this core level which impacts on the accuracy of the peak deconvolution.[24]

The effect of annealing the $(NH_4)_2S$ treated GaAs surface, *in situ* in different environments, was also investigated. Figure 4 shows the (a) As $2p$, (c) Ga $2p$, (d) O $1s$, and (e) S $2p$ spectra from $(NH_4)_2S$ treated surfaces with subsequent anneal in UHV, forming gas, and N_2 at 500 °C. All anneals are seen to remove the As oxides to within detection limits of XPS, as well as decrease the states associated with the gallium oxide states. In fact, from the O $1s$ spectra after the vacuum and N_2 anneal, the concentration of oxygen is below XPS detection limits. This suggests the residual states seen in the Ga $2p$ spectra on these samples are due solely to Ga-S bonding. This is also reflected in the S $2p$ spectra, where the lowest concentration of sulfur is seen on the vacuum annealed surface, highlighted further by the ratio of the calculated peak area from the fitted S $2p$ and Ga $3s$ peaks, seen in Figure 4(f). Due to the similarity of electronegativites, it is usually difficult to discern Ga-S from the Ga_2O state, and as such for the $(NH_4)_2S$ treated and forming gas anneal (FGA) samples in Figure 4(c), where an oxygen signal is seen in the O $1s$ spectra, the peak labeled Ga_2O is due to a combination of both of these states.

The As-As and As- states in the As $2p$ spectra in Figure 4(a) are also seen to vary as a function of annealing condition, with the ratio of their fitted peak areas to that of the bulk peak showing this more clearly in Figure 4(b). The vacuum and N_2 annealed surfaces show no evidence of As-As; however, As- states are seen to emerge, particularly on the vacuum annealed surface. This could correlate to the absence of oxygen on the surface, with the increased level of sulfur remaining on the N_2 annealed surface mitigating the formation of As- states. On the FGA sample, there is still possible evidence of As-As states; however, the concentration is close to the detection limit associated with XPS peak fitting.

Previous reports have suggested that the As-As state forms as a result of growth of the native oxides on the (In)GaAs surface.[4] Therefore, it may be possible to further diminish the impact of these states by minimizing the atmospheric exposure time of the semiconductor samples after $(NH_4)_2S$ treatment and prior to ALD pre-treatment, as recently reported.[25] The results presented here suggest that, for GaAs, *in situ* annealing in N_2 at 500 °C prior to ALD may be able to fully remove As-As states from the surface and still retain an appreciable S coverage, which can suppress the formation of arsenic dangling bonds when compared to a vacuum anneal.

In conclusion, we have shown that by utilizing multiple cycles of TMA prior to Al_2O_3 deposition, it was possible to decrease the concentration of As-As states that were detected at the Al_2O_3/(In)GaAs interface. This suggests that pretreatments with TMA, prior to high-k dielectric deposition, may be an effective method to improve InGaAs device performance,[11,25,26] which are possibly correlated to the concentration of As-related defects.[4,5] *In situ* annealing of the $(NH_4)_2S$ treated GaAs surface prior to oxide deposition has also been shown to decrease the concentration of As-As states to within detection limits of XPS.

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