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Interface Between Atomic Layer Deposition Ta_2O_5 Films and GaAs(100) Surfaces

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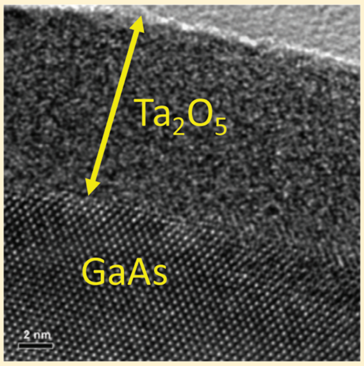
ABSTRACT: Ta_2O_5 films were deposited on GaAs(100) surfaces using thermal atomic layer deposition from pentakis dimethyl amino tantalum (PDMAT) and H_2O. The interface between the films and native oxide covered GaAs surfaces has been examined using X-ray photoelectron spectroscopy as a function of film thickness and for deposition temperatures ranging from 200 to 350 °C. Gradual removal of the surface arsenic and gallium oxides was observed, with the removal of the arsenic oxides in general more efficient. The high oxidation states of both the arsenic and the gallium oxides were also found easier to remove. Elevation of the process temperature above 300 °C resulted in significant enhancement of the native oxide removal rate. When films were deposited on GaAs surfaces that had the surface oxides removed, a practically sharp interface between the film and the GaAs substrate was maintained.



■ INTRODUCTION

Widespread use of GaAs in the semiconductor industry has been hindered in the past by the absence of a high-quality native oxide. However, the introduction of high dielectric constant (high-*k*) films as a possible replacement for SiO_2 in Complementary Metal Oxide Semiconductor (CMOS) devices and the vast literature created that has documented issues pertaining to the formation of interfacial layers and poor carrier mobility have led to a renewed interest in this material. Functional devices with high-*k* gate oxides on GaAs have been successfully demonstrated, using mainly atomic layer deposition (ALD) as the technique of choice for the deposition of the dielectric.[1−5] At the same time, several reports documented a so-called "interface cleaning" reaction during the ALD of HfO_2 and Al_2O_3 on GaAs and InGaAs surfaces. Deposition of the film using a starting surface covered with native gallium and arsenic oxides resulted in the consumption of the surface oxides and the formation of a practically sharp interface.[6−9] This observation is noteworthy since similar depositions on hydrogen-terminated Si surfaces invariably resulted in the formation of a SiO_2-based interfacial layer.[10] These reports led to extensive investigation of these ALD processes and the surface chemistry they entailed. For the HfO_2 ALD, two amine variants of the precursor (TEMAH and TDMAH) were shown to have similar behavior.[9,11,12] Although there were conflicting reports[13,14] for similar HfO_2 ALD processes, Suri et al.[15] demonstrated that the process temperature may account for some of these observations. At the same time, another precursor of the same family, tetrakis dimethyl amino titanium (TDMAT), was also shown to result in an interface cleaning reaction during the thermal ALD of TiO_2 on GaAs,[16] indicating that the common thread for some of these observations is the use of similar precursors that belong to the amide family.

While there is the expectation that transition metal precursors will behave similarly in thermal ALD processes, this is far from obvious as recent results have shown that even precursors featuring metal atoms from the same group can behave differently in similar processes. A prime example that demonstrates how little these processes are currently understood is the case of $HfCl_4$ and $TiCl_4$ precursors in thermal ALD using H_2O as the oxidizing agent. Both precursors are very similar in structure and have group IV transition metals as the central atom. However, when HfO_2 was deposited on native oxide GaAs surfaces, Delabie et al. observed removal of the native oxides,[14] while Frank et al. did not observe such an occurrence.[7] In a recent study, Granados-Alpizar and Muscat showed that $TiCl_4$ removes O from the surface and leaves it passivated with Cl that inhibits growth of TiO_2 films even after 50 ALD cycles at process temperatures as high as 230 °C.[17] By contrast, both Frank[7] and Delabie[14] report normal ALD growth of HfO_2 on GaAs from $HfCl_4$ and H_2O. These observations indicate that even though the general consensus is that precursors of the same family will have similar chemistry this is not always true, and generally speaking conclusions for one member of the precursor family should not be generalized. To this date, there is no first-principles computational treatment of the metal chloride/GaAs and metal amine/GaAs system, although a recent computational study using DFT by Sylwia Klejna and Simon D. Elliott has been published for the interaction of trimethyl aluminum with GaAs surfaces.[18]

In this manuscript, we introduce a new GaAs "interface cleaning" ALD process that utilizes an amide precursor featuring a group V transition metal atom, Ta. We used pentakis dimethyl amino tantalum (PDMAT) and H_2O to deposit Ta_2O_5 films on native oxide GaAs surfaces and studied the evolution of the interface as a function of film thickness and

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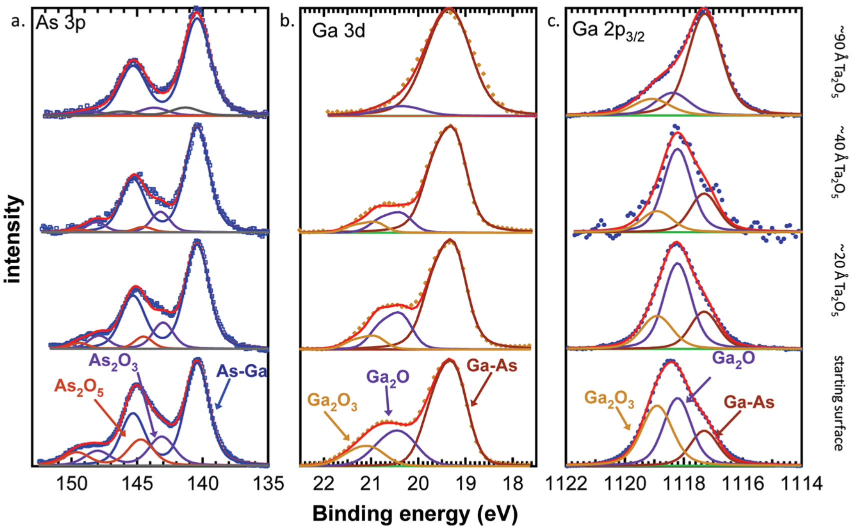

Figure 1. As 3p, Ga 3d, and Ga $2p_{3/2}$ XP spectra for the starting (native oxide covered) surface GaAs(100) and after deposition of 20, 40, and ~90 Å Ta_2O_5 at 250 °C. Gradual removal of the surface gallium and arsenic oxides is observed. The 90 Å film was thinned in the analytical chamber prior to the data acquisition.

deposition temperature. Being a member of group V, Ta and consequently its amine precursor have significantly different electronic structure than the Hf and Ti amines that were used in earlier work.[9,11−16] Ta_2O_5 is a very good high-*k* dielectric, and it was shown recently that when used as a gate dielectric in AlN/GaN High Electron Mobility Transistors it results in devices with significantly improved properties over similar devices utilizing HfO_2 gate dielectric.[19,20] The ability to obtain and maintain a sharp interface between Ta_2O_5 and GaAs as demonstrated in this manuscript may have significant implications in the development of III−V semiconductor technology.

■ EXPERIMENTAL DETAILS

Ta_2O_5 films were deposited using a thermal ALD process in a flow-type hot-wall ALD reactor described elsewhere.[21] Pentakis dimethyl amino tantalum (PDMAT) was used as the Ta source and H_2O as the oxidizing agent. The metal organic precursor was kept in a stainless steel bubbler and heated at ~110 ± 2 °C to ensure a high enough vapor pressure. Process optimization was performed using films deposited on cleaned native oxide Si(100) surfaces, and the ALD process window obtained was pretty similar to the one reported by Maeng at al. for a similar thermal process using the same precursor.[22] The measured growth rate was ~0.6 Å/cycle, in good agreement with other literature reports for similar thermal ALD processes.[22−24] The native oxide GaAs(100) surfaces used in this work were prepared by cleaning the substrates in acetone and methanol, followed by a deionized water rinse and N_2 blow dry. GaAs surfaces were stripped of their native oxide using a NH_4OH-based procedure which has been shown to remove all but traces of the surface arsenic and gallium oxides.[25] After etching, the substrate was transferred to the reactor immediately, and a film was deposited. For each sample deposited on GaAs surfaces, a companion Si sample was also prepared to facilitate accurate measurement of the film thickness and to verify process reproducibility. Film thickness was routinely measured using a Woollam alpha-SE fixed-angle spectroscopic ellipsometer (SE).

The film/GaAs interface was examined using ex situ X-ray photoelectron spectroscopy performed with a Kratos AXIS 165 spectrometer (Al X-ray source, 1486.6 eV), equipped with a hemispherical analyzer (165 mm radius). The samples did not undergo any sputter cleaning prior to analysis. High-resolution spectra of the As 3p, Ga 3d, and Ga $2p_{3/2}$ regions were recorded at 0.1 eV step size, 20 eV pass energy, and with photoelectron emission normal to the sample surface. After baseline correction, Gaussian−Lorentzian peaks were used to estimate the contribution of the various oxidation states for each region. The Lorentzian peak full width at half-maximum (fwhm) was set at 40% of the Gaussian fwhm for all peaks. The As $3p_{3/2}$ and $3p_{1/2}$ doublet region is fairly complex as the substrate and various As oxide peaks overlap partially. The analysis of this region was performed using functions of equal Full Width at Half Maximum (fwhm), a spin−orbit separation of 4.9 eV, and intensity ratio of 2:1, and the substrate As $3p_{3/2}$ peak (As−Ga) was placed at a binding energy of 140.4 eV. The arsenic oxide contribution was estimated using separate doublets for the As^{3+} (As_2O_3) state (chemical shift: +2.9 ± 0.1 eV), As^{5+} (As_2O_5) state (chemical shift: + 4.5 ± 0.1 eV), and an arsenic suboxide−metallic arsenic component As^0−AsO_x (chemical shift: +0.8 ± 0.2 eV).[26] The Ga 3d region was analyzed using doublets of the same fwhm, 0.44 eV spin−orbit splitting, and peak ratio of 3:2. The Ga $3d_{5/2}$ peak for the substrate was placed at 19.2 eV, and the chemical shifts used were +1.3 ± 0.1 eV for the Ga^{1+} (Ga_2O) component and +1.9 ± 0.1 eV for the Ga^{3+} (Ga_2O_3) state.[27,28] The Ga $2p_{3/2}$ region was analyzed by using three peaks: the substrate peak was placed at 1117.3 eV, the Ga^{1+} state had a chemical shift of +1.0 ± 0.1 eV, and the Ga^{3+} state had a chemical shift of +1.7 ± 0.1 eV.[27,28] The chemical shifts used for the Ga oxides in the 3d and $2p_{3/2}$ regions were found to give a consistent distribution of the Ga^{1+} and Ga^{3+} concentrations between the two regions. Charge compensation was performed using the binding energies for the As 3p substrate peaks and the adventitious C 1s peak. It is noted that the most frequently used As 3d peaks were not utilized for this work as they overlap with the Ta $5p_{1/2}$ and a Ta loss peak, making analysis of the region very hard.[29,30]

Bright field transmission electron microscopy (TEM) and HRTEM data were provided by TEM Analysis Services Lab. The samples were prepared by conventional TEM sample preparation methods using Ar ion beam milling. Bright field imaging was performed using a Philips 420 TEM at 120 KV, and the HRTEM images were obtained with an FEI Tecnai instrument at 200 KV.

■ RESULTS

The starting native oxide GaAs surfaces were characterized using XPS and transmission electron microscopy. Bright field images of the starting surface have shown the native oxide to be ~25 Å in thicknes, and XPS composition analysis has shown this native oxide to be gallium rich (Ga:As ~ 1.3) In this starting surface, there are twice as many gallium atoms as arsenic. Such observations are in agreement with prior observations for thermal and native GaAs oxides that have been shown to be consistently Ga rich.[31,32] The composition of thick Ta_2O_5 films was also examined by XPS, and they were found to be slightly overoxidized with a O/Ta ratio of ~3. Metal oxide films are known to react with the ambient moisture, and these films were exposed to air and were not sputter-cleaned prior to the analysis. Earlier work by Kukli et al. has reported the presence of TaO_2 in tantalum oxide films grown by ALD using $TaCl_4$ and H_2O as precursors.[33] We have found no evidence for the presence of TaO_2 in our films.

A series of films with varying thickness were deposited at the optimum ALD temperature of 250 °C on native oxide GaAs(100) surfaces, and the composition of the interface was examined by XPS. Figure 1 shows the As 3p, Ga 3d, and Ga $2p_{3/2}$ regions for the starting native oxide GaAs(100) surface and after depositing 20, 40, and 90 Å of Ta_2O_5. To facilitate comparison, the spectra for each region have been normalized. After analyzing each spectral region in its components and comparing the spectrum for the starting surface with those for the 20 and 40 Å films, it is evident that there is removal of both the arsenic and gallium oxides from the interface. More specifically, for the arsenic oxides, deposition of the 20 Å film results in a substantial decrease of the As_2O_5 concentration and a small but observable decrease in the As_2O_3 concentration. When the film grows to 40 Å, very little As_2O_5 and about 1/3 of the initial As_2O_3 is observed. For the gallium oxides, there is a distinct difference between the starting surface and after the film deposition. Deposition of 20 Å of Ta_2O_5 results in a decrease in the Ga^{3+} content and increase of the Ga^{1+} component. Deposition of 40 Å of TA_2O_5 results in an overall decrease in the intensity of both Ga oxidation states. For both films, the ratio of the intensity of both Ga oxidation states to the substrate decreases with the Ta_2O_5 film thickness. The 90 Å film had to be sputter-thinned in the analytical chamber to allow observation of the interface. Care was exercised to retain some of the Ta_2O_5 film to protect the integrity of the interface. The peak broadening observed for this sample is attributed to damage induced by the Ar ion sputtering process.[34,35] Regardless of that, there is marked reduction in the intensity of all oxide peaks between the 40 and 90 Å films, and only traces of the As^{3+}, Ga^{3+}, and Ga^{1+} states remain at the interface after the 90 Å (150 cycles) deposition.

Overall, the best metric to describe the removal of the surface oxides during the deposition is the ratio of the oxides to the substrate peak areas. The intensity of each peak decreases exponentially with the Ta_2O_5 film thickness, and as a result the ratio is independent of the thickness of the Ta_2O_5 film. If one assumes that the thickness of the interfacial oxide remains constant regardless of the Ta_2O_5 thickness, this would lead to the conclusion that the ratio of the oxide peak intensity to the substrate peak intensity should also remain constant. If the deposition of the Ta_2O_5 is accompanied by growth of the interfacial oxide, then the ratio would increase as well. The fact that we observe a reduction in the ratio of the surface oxide to the substrate peak area indicates that part of the surface gallium and arsenic oxides have been removed during the deposition. This argument assumes that the native gallium and arsenic oxides form a homogeneous layer. It appears that in the case of both the arsenic and the gallium oxides we initially have conversion of the high oxidation state (the As^{5+} and Ga^{3+}, respectively) into the lower oxidation state (the As^{3+} and Ga^{1+}) and subsequent removal of this state from the interface.

The removal of the native oxides during the film growth is verified by the TEM data presented in Figure 2. A 150 cycle film was deposited at 250 °C on a cleaned native oxide GaAs(100) surface similar to that used for the films included in Figure 1. The bright field image of Figure 2a shows that the film thickness is ~9 nm which is in good agreement with the expected thickness from the measured growth rate. Images 2b, c, and d show different regions of the substrate−Ta_2O_5 interface and verify the practically complete removal of the starting ~25 Å of surface native oxides. These images also indicate that the Ta_2O_5 film is homogeneous and amorphous but the interface looks somewhat rough.

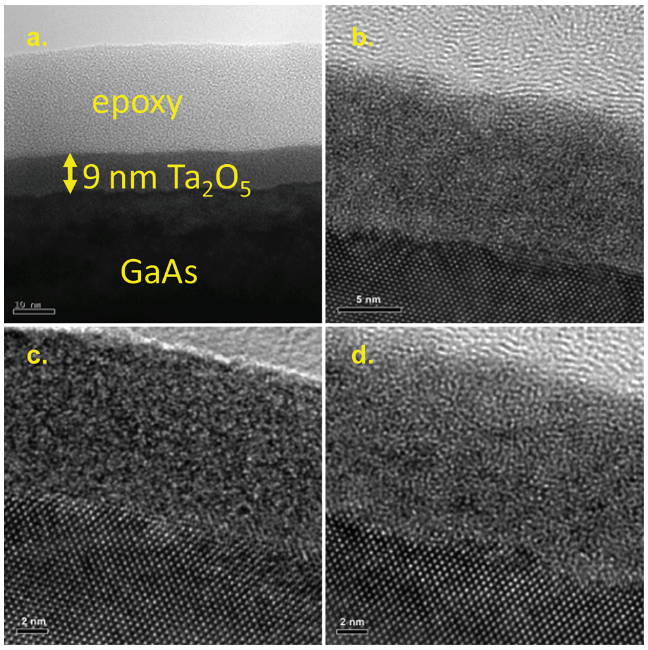

Figure 2. Bright field image and high-resolution transmission electron microscopy data for a ~90 Å Ta_2O_5 film deposited on a native oxide covered GaAs(100) surface. A practically sharp interface is obtained between the GaAs substrate and the Ta_2O_5 film.

The composition of the interface for films deposited on GaAs surfaces that have been stripped of the native oxide has also been examined for a ~30 Å Ta_2O_5 film that was deposited at 250 °C. The sample was examined using XPS, and the data presented in Figure 3 indicate that a practically sharp film/substrate interface is obtained with only trace amounts of arsenic and gallium oxides; the equivalent of about a monolayer of Ga_2O remains at the interface.

To test the effect of the deposition temperature on the efficiency of the interface cleaning reaction, two sets of films

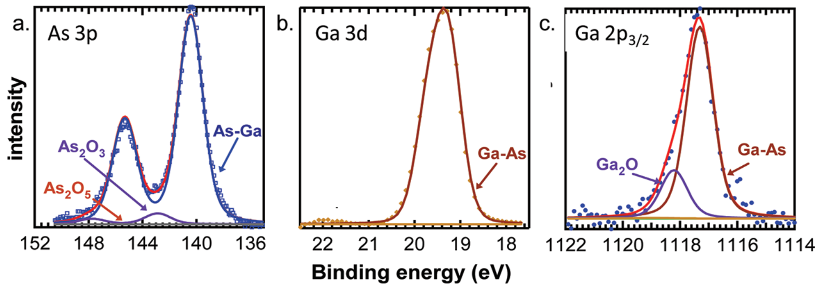

Figure 3. XP spectra after the deposition of ~30 Å of Ta_2O_5 deposited on an etched GaAs surface. A practically sharp interface between the Ta_2O_5 film and the GaAs substrate is maintained.

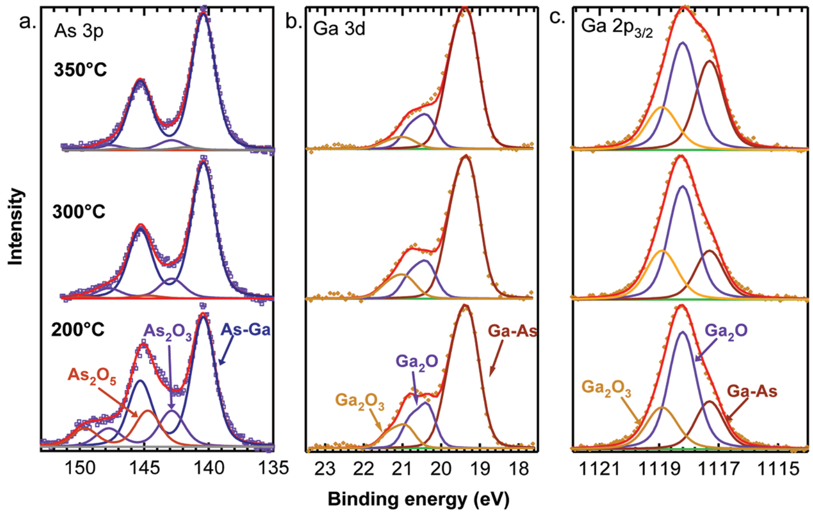

Figure 4. XP spectra for ~2 nm Ta_2O_5 deposited on native oxide GaAs(100) surfaces at 200, 300, and 350 °C. Elevation of the deposition temperature enhances the native oxide consumption reaction.

with thickness ~2 and ~3 nm were prepared at 200, 300, and 350 °C. These temperatures lie outside the ALD window. The interfaces were examined using ex situ XPS, and the results are shown in Figures 4 and 5, respectively. The film thickness was chosen so that the interface could be examined without the need to sputter some of the Ta_2O_5 film. Comparing the 2 nm films deposited at 200 and 300 °C (Figure 4), we can see that the increase in the process temperature results in almost complete removal of the As_2O_5 oxide and a substantial reduction in the intensity of the As_2O_3. However, for the gallium oxides, no substantial effect is observed. When the deposition temperature is further increased to 350 °C, then a clear change in the composition of the interfacial oxides is observed: most of the arsenic oxides are removed, and there is a very substantial reduction in the amount of gallium oxide remaining in the interface as evidenced by both the Ga 3d and Ga $2p_{3/2}$ spectral regions. The findings are similar for the 3 nm films (Figure 5), and when comparing the 2 and 3 nm films deposited at the same temperature, one can see that for the thicker film less of the surface oxides remains at the interface. The removal of the arsenic and gallium oxides seems to be a gradual process that continues for several ALD cycles, similar to what is observed for the films in Figure 2. The variation in the composition of the interface oxides for the 2 nm films indicates that these films are thick enough to protect the interface from postdeposition reoxidation.

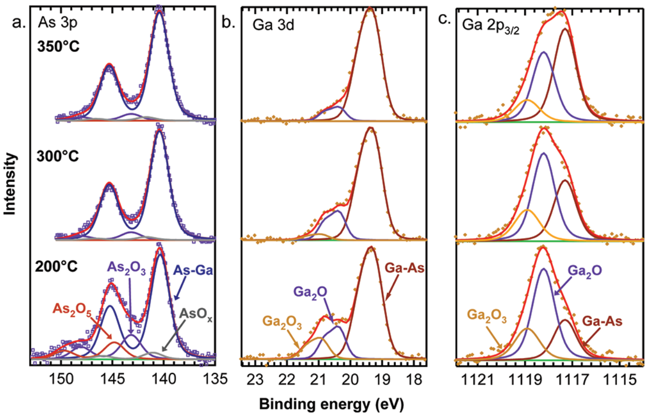

Figure 5. XP spectra for ~3 nm Ta_2O_5 deposited on native oxide GaAs(100) surfaces at 200, 300, and 350 °C. Elevation of the deposition temperature enhances the native oxide consumption reaction.

■ DISCUSSION

When Ta_2O_5 films are deposited on native oxide covered GaAs(100) surfaces, removal of the surface gallium and arsenic native oxides is observed. Arsenic oxides are found easier to remove, while the removal of the gallium oxides is less efficient. The XPS data in Figures 1, 4, and 5 and the TEM data in Figure 2 suggest that the removal of the surface native oxides is a gradual process that may take several cycles to complete. For example, there is a substantial reduction in the intensity of the gallium and arsenic oxides between the starting surface and after deposition of 20 Å of Ta_2O_5. This trend continues for the 40 Å film, but even at this Ta_2O_5 film thickness a substantial concentration of gallium oxides and some arsenic oxide are still detected at the interface. The XPS and HRTEM data for the 90 Å film show a practically sharp interface, indicating that the film growth from 40 to 90 Å was probably accompanied by continuous removal of the remaining surface native oxides. The observed gradual removal of the surface native oxides and the persistence of the gallium oxides at the interface mirror earlier observations for other ALD processes that utilized amine precursors, such as: HfO_2 deposition from TEMAH/H_2O[36] and TDMAH/H_2O[15] and TiO_2 deposition from TDMATi/H_2O.[16]

Assuming a simple ligand substitution mechanism, the ALD reaction byproduct would be dimethyl amine $(CH_3)_2NH$. We hypothesize that the dimethyl amine ALD reaction product is responsible for the native oxide etch. We base this assumption on the fact that:

(i) similar observations have been made for other amine-based ALD processes and
(ii) the thermal decomposition of amine metal organic species such as tetrakis dimethyl amino arsenic (TDMAAs) and tetrakis dimethyl amino antimony (TDMASb) have been routinely used for in situ cleaning of III–V semiconductors from the surface oxides.[37−39]

Then, to explain the observed gradual removal of the interface oxides, we need to stipulate that either (i) the amines diffuse through the metal oxide film, react at the interface to produce arsenic and gallium amines, and then have these species diffuse in the gas phase through the T_2O_5 layer or (ii) the arsenic and gallium oxides "bubble" through the Ta_2O_5 film to the surface and react with the ALD produced amines thereafter. While there are reports of arsenic oxides "bubbling" through an ALD HfO_2 overlayer, no such observations have been made for gallium oxides.[9] As a result we have to assume that such diffusion processes occur through 2−4 nm thick Ta_2O_5 films. Diffusion of species through solid films several nanometers thick has been reported in a number of studies: A small sample includes the following examples:

(i) In the deposition of manganese on Si, diffusion of species through the film is used to explain the experimental observations;[40,41]
(ii) Si diffusion through La_2O_3 films spanning several tens of nanometers[42] as well as diffusion of O, Ga, and As through SiN_x and SiO_xN_y on GaAs have been observed;[43]
(iii) The high-*k* literature is full of examples on interfacial oxidation when several nanometer thick stacks on Si are annealed in the presence even of low O_2 concentrations.[44−48]

Interface cleaning reactions have also been observed for the ALD of Al_2O_3 from TMA and H_2O. In situ observation of the surface reactivity indicates that the first TMA pulse is mainly responsible for the arsenic oxide removal.[17,32,49] Recently, Tallarida et al.[50] have demonstrated that the first two TMA pulses reduce the vast majority of the As^{3+} surface species into As suboxides that are subsequently removed from the interface. Contrary, for the Ga^{3+} oxides, they observe a slower and almost linear reduction of the species intensity for the first six pulses. This significantly slower removal of the gallium oxides has also been confirmed by Lee et al. for the same ALD chemistry.[32]

The high oxidation states for both As (As^{5+}) and Ga (Ga^{3+}) are removed faster, and the removal of all the arsenic oxides is in general more efficient than the removal of the gallium oxides for depositions performed from 200 to 350 °C. The faster removal of the higher arsenic oxidation state (As^{5+}) has been observed for most of the amine-precursor ALD processes referenced above. Hinkle at al. used a coordination argument to explain this finding for HfO_2 ALD. These authors suggested that the precursor reacts preferentially with the As^{5+} state as Hf atoms prefer the high coordination configuration.[11] As a result, the As^{5+} state is removed more easily even though it is thermodynamically more stable than the As^{3+} state; the standard heat of formation for As_2O_5 is ∼915 vs ∼655 kJ/mol for As_2O_3.[51,52] However, a different explanation may be suggested by invoking two other possible reaction pathways that may convert As_2O_5 into As_2O_3 at temperatures below 300 °C.[53−55] These pathways involve either a reaction with the substrate

$$4GaAs + 3As_2O_5 \rightarrow 2Ga_2O_3 + 3As_2O_3 + 4As \tag{1}$$

or a direct thermal decomposition reaction

$$As_2O_5 \rightarrow As_2O_3 + O_2 \tag{2}$$

Reaction 1 results in the consumption of As_2O_5 and the formation of elemental As and Ga_2O_3. For the 20 and 40 Å films deposited at 250 °C (Figure 1), within the accuracy of the fit we did not observe a substantial increase in the As concentration. Some traces of arsenic suboxide and/or elemental arsenic can be detected at the 90 Å film; however, they correspond only to a small fraction of the initial As^{5+} intensity. Arsenic desorption is known to be relatively slow at 250 °C,[56−58] so the XP signal should be directly proportional to the arsenic concentration at the interface. However, analysis of this region is challenging due to the partial overlap of the substrate and the oxide peaks that may obscure the presence of low intensity peaks. Further insight for the relative importance of reaction 1 can be gained from inspection of the Ga $2p_{3/2}$ peak. Comparison of the Ga $2p_{3/2}$ peaks for the starting surfaces to that for the 20 and 40 Å films shows a clear decrease in the peak width indicating net removal of the Ga^{3+} component. On the basis of the above, it appears that for depositions at 250 °C reaction 1 should represent a minor channel and that removal of the As^{5+} (As_2O_5) should be due to thermal decomposition described by reaction 2. The conversion of As^{5+} to As^{3+} although thermodynamically not favorable can be explained in terms of the principle of mass action: continuous evolution of the O_2 product would result in the conversion of the As^{5+} into As^{3+}.[53]

Additional evidence for the importance of reaction 2 has been offered recently by Brennan and Hughes; they have shown that for InGaAs surfaces the As^{5+} state converts into As^{3+} at temperatures as low as 150 °C in a vacuum with no overall As loss.[59] At 300 °C in vacuum the conversion is practically complete, and at higher temperatures removal of the As^{3+} state is observed. The same authors have verified that for temperatures below 300 °C the desorption of the arsenic oxides is insignificant and that there is no exchange of oxygen between the As and the Ga, providing some additional evidence that contribution of reaction 1 is likely very small for the films deposited in that thermal range. These finding are reflected in similar earlier observations by Ingrey et al. that have shown removal of the As^{5+} oxides from GaAs surfaces during vacuum anneals below 250 °C and significant removal of the As^{5+} and

As^{3+} oxidation states at 320 °C. An arsenic suboxide has been detected to remain on the surface though up to 380 °C.[60]

Temperature can have a significant effect on the overall efficiency of each reaction and the relative importance of each reaction channel. The data in Figures 4 and 5 indicate that when the deposition temperature is increased from 200 to 300 and 350 °C there is enhancement in the removal of the arsenic oxides. The fact that the volatility of the various arsenic oxides, especially As_2O_5, increases with temperature may account for at least part of the observed effect. However, As_2O_3 is not very volatile below 300 °C,[59,60] so reactions of the arsenic oxides with the precursors and the ALD reaction byproducts should account mainly for these observations. Additionally, there is evidence for the reaction mechanism with the precursor and/or ligands by the observed removal of the arsenic oxides for TiO_2 ALD from TDMAT and H_2O at 200 °C; at this temperature, the effect of desorption especially for the As_2O_3 should be negligible.[16]

For the gallium oxides, no significant difference is observed between 200 and 300 °C, but increasing the temperature to 350 °C results in a significant reduction in the intensity of the gallium oxides at the interface. Gallium oxides are not desorbed from the surface at that temperature range, so any reduction in their intensity should be a result of reactions during the ALD process.[60] The overall picture is further complicated by considering the following findings: when GaAs native oxide surfaces were subjected to anneals at 320 °C, Lee et al. demonstrated loss of the As oxide that resulted in an almost equal increase in the gallium oxides, indicating that at least at that temperature reaction 1 can have a significant effect.[32] For temperatures between 320 and 400 °C, an additional pathway that converts As_2O_3 into Ga_2O_3 is possible[61]

$$2GaAs + As_2O_3 \rightarrow Ga_2O_3 + 2As_2 \qquad (3)$$

Although reactions 1 and 3 are known to produce Ga_2O_3, the experimental data indicate that the Ga^{3+} (Ga_2O_3) state is removed faster than the Ga^{1+} state and that possibly Ga_2O_3 is converted into Ga_2O before it is removed from the interface. This observation is in agreement with similar observations for the HfO_2/GaAs interface.[36] Thermodynamically, this conversion is not favored as Ga_2O_3 ($\Delta H^0 \sim 1090$ kJ/mol) is more stable than Ga_2O ($\Delta H^0 \sim 356$ kJ/mol for Ga_2O) at room temperature.[62] There is a substrate reaction that can convert Ga_2O_3 into Ga_2O, but it is thought to require temperatures in excess of 500 °C. Ga_2O is volatile at that temperature, resulting in its desorption from the surface.[61] At the temperature range used in this work (200−350 °C), the various gallium oxides are not volatile,[60] so any removal that is observed should be the result of reactions with the precursor and/or the ligands liberated through the ALD reaction.

The surface chemistry of GaAs and its native oxides is fairly complex with several possible reactions between the various species. The fact that the surface temperature may alter the relative importance of the various reaction pathways adds to the complexity. In light of the observations listed before, it is likely that the removal of the arsenic oxides from the interface is the result of several different processes that involve conversion of the As^{5+} state into As^{3+} and then either reaction of the As^{3+} with the amines produced during the ALD reaction or further reduction of the As^{3+} into As suboxides and then subsequent removal from the interface through reaction with the same amines. Combining our work with the observations by Lee et al.[32] and Brennan et al.,[59] we can suggest that for temperatures up to 300 °C (i) the As^{5+} state is primarily removed via thermal decomposition into the As^{3+} state as described by reaction 2, (ii) the transfer of oxygen from the As to the Ga species described by reaction 1 is insignificant, and (iii) the As^{3+} and the Ga^{3+} and Ga^{1+} states are removed via a reaction that involved the precursor and/or the ALD reaction byproducts. For temperatures in excess of 300 °C, (i) desorption may aid in the removal of the arsenic oxides, and (ii) reaction 1 may contribute to the consumption of the arsenic oxides and provide an additional source of gallium oxides. Nonetheless, removal of the gallium oxides is also enhanced due to the elevated process temperature.

The significant enhancement observed for the interface cleaning reaction due to elevated process temperature indicates that the reactions involved are thermally activated. Similar observations have been made for the TMA/H_2O[49] and TDMAH/H_2O ALD processes.[15] Again, although the removal reaction is enhanced, still a substantial concentration of Ga^{1+} and some Ga^{3+} remains at the interface even after the deposition of 3 nm of Ta_2O_5 at 350 °C. Ga^{1+} (Ga_2O) is the more persistent of the two Ga oxidation states and is detected at approximately a monolayer level even for the film deposited on etched GaAs surfaces. Ga_2O has been shown to persist at the interface for the majority of the ALD chemistries known for their interface cleaning effects,[36,16] but it has been shown that these states do not contribute to the Fermi level pinning.[63−65] It has been suggested that these states when located at the interface may provide the bridge for the formation of the other states including high-k dielectrics facilitating the formation of a high-quality interface.[59]

When films were deposited in etched GaAs surfaces, we found that this could be accomplished without the regrowth of arsenic and gallium oxides. This is particularly noteworthy as growth of Ta_2O_5 films on hydrogen-terminated Si surfaces using a variety of depositions is invariably accompanied by the formation of a SiO_2-based interfacial layer.[66,67]

■ CONCLUSIONS

The ALD of Ta_2O_5 films on GaAs(100) from PDMAT and H_2O results in the gradual consumption of the surface native gallium and arsenic oxides. This process adds one more amine precursor based ALD process for which an "interface cleaning" reaction is observed. Arsenic oxides are easier to remove than gallium oxides. Although they are expected to be more stable from a thermodynamic point of view, the higher oxidation states of both arsenic (As^{5+}) and gallium (Ga^{3+}) are easier to remove. Elevating the process temperature results in faster removal of all oxides. Deposition of Ta_2O_5 on etched GaAs(100) surfaces results in a practically sharp interface with about a monolayer of Ga_2O remaining.

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Notes

The authors declare no competing financial interest.

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