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Reduction of native oxides on GaAs during atomic layer growth of Al_2O_3

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The reduction of surface "native" oxides from GaAs substrates following reactions with trimethylaluminum (TMA) precursor is studied using medium energy ion scattering spectroscopy (MEIS) and x-ray photoelectron spectroscopy (XPS). MEIS measurements after one single TMA pulse show that ~65% of the native oxide is reduced, confirmed by XPS measurement, and a 5 Å thick oxygen-rich aluminum oxide layer is formed. This reduction occurs upon TMA exposure to as-received GaAs wafers. © *2009 American Institute of Physics*. [DOI: 10.1063/1.3148723]

The integration of high-*k* dielectrics with high mobility III-V semiconductors is important due to the need for higher speed and lower power electronic devices than what are offered by Si-based technologies. Among III-V semiconductors, GaAs and InGaAs are promising substrates for high-*k* dielectric deposition.[1–3] The removal of native oxides and the growth of an ideal dielectric layer on GaAs and InGaAs remain a serious challenge. This obstacle arises in part from the high density of defects present at most GaAs-dielectric interfaces, which leads to Fermi-level pinning at the interface.[4,5] Several groups have shown that chemical cleaning and subsequent passivation of Ge and GaAs (for example, with ammonium sulfide) prior to dielectric deposition can greatly reduce the interface state density (D_{it}) (Refs. 6 and 7). However, few passivation solutions are practical for future large scale complementary metal-oxide semiconductor device manufacturing. Although several studies have shown the reduction of native oxides on GaAs and InGaAs during atomic layer deposition (ALD) of dielectrics,[1,8,9] detailed structural and chemical information about the interface and reduction process have not been reported. We have examined depth profiles of the elements in native oxides and ALD-deposited Al_2O_3 layers on GaAs substrates with an integrated tool that enables ALD growth with *in situ* characterization by medium energy ion scattering spectroscopy (MEIS). Films were also analyzed by x-ray photoelectron spectroscopy (XPS), *ex situ*. Our methods allow us to determine, with high depth resolution, the composition, structure, and chemistry of this multilayer system as the dielectric is grown.

In this work, *p*-type GaAs (Zn-doped) substrates were mounted as received in the ALD chamber, leaving the native oxides intact. The substrate was first heated to 320 ± 15 °C under vacuum for about 30 min to remove moisture and surface hydrocarbons. The sample was then transferred under ultrahigh vacuum (UHV) to the MEIS analysis system (base pressure 6×10^{-10} Torr). Medium energy ion scattering spectroscopy (MEIS) determines the absolute number (areal density) and mass of atoms. Depth profiles of the elements were obtained by computer simulation of the backscattered ion energy distributions. In this study, a 130 keV proton beam was used. After the MEIS measurement, the sample was transferred back to the ALD chamber and reheated to 320 °C, and was followed by a 2 s pulse of trimethylaluminum (TMA) precursor. At the end of each TMA exposure, 5 min of cyclically evacuating and purging (N_2, ~7 torr) the growth chamber ensured the removal of residual precursor gas. The sample was then re-examined by MEIS. The procedure was repeated after an additional three TMA pulse exposure. XPS spectra were taken with a Perkin-Elmer hemispherical analyzer with a nonmonochromatic Al $K\alpha$ x-ray source ($h\nu = 1486.6$ eV). At 17.9 eV pass energy, the full width at half maximum (FWHM) of the Cu $2p$ 3/2 core level is 1.2 eV. All core level photoemission peaks were referenced to the As $3d$ 5/2 level for unoxidized GaAs (40.5 eV) to compensate for any effects of charging in the overlayer. Peak fitting for the As $3d$ and Ga $3d$ core levels includes the contributions from the spin-orbit splitting and the broadening of each oxide peak. The FWHM values of the fitted peaks (which also take into account our instrumental broadening) are 1.2 eV for GaAs (for both As $3d$ and Ga $3d$), 1.3 eV for As oxides and 1.4 eV for Ga_2O_3.

Figure 1(a) shows a comparison of MEIS data from a GaAs sample after preheating at 320 °C and after the initial TMA pulse exposure. The formation of an AlO_x layer is clearly observed as has previously been reported[10] as well as the reduction in the Ga and As peaks after the TMA exposure. The resulting depth profiles [Fig. 1(b)] for the preheated sample can be modeled with a 10 Å native oxide layer that is Ga rich (Ga/As = ~2.3). The TMA-exposed sample prior to additional oxygen (water) exposure, already shows several interesting features. First, a 5 Å thick oxygen-rich $Al_2O_{3.4}$ layer is formed. This is unexpected considering that Al_2O_3 is often grown in ALD by alternating TMA and water pulses. This Al oxide layer formation without an oxygen source suggests that the oxygen uptake comes from a reduction in the native oxide. We observe a reduction in the thickness of this oxide from 10 to 7 Å which supports this conclusion. The O aerial density in the native oxide is reduced from approximately 4.6×10^{15} to 1.6×10^{15} atom/cm^2 while the O density in the aluminum oxide is 3.5×10^{15} atom/cm^2. There is a small partial pressure of O_2 and H_2O in the ALD system (not under UHV conditions) such that an additional 0.5×10^{15} atom/cm^2 of oxygen is added to the film during growth (in addition to that present in the native oxide), possibly in the form of physisorbed water

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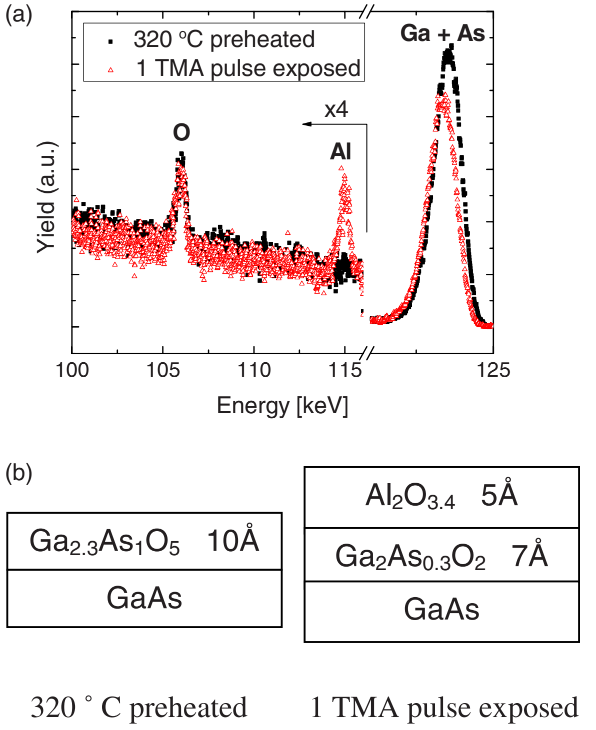

320 ° C preheated 1 TMA pulse exposed

FIG. 1. (Color online) (a) MEIS spectra for a GaAs sample taken after preheating at 320 °C for ~30 min, and after exposure to one TMA pulse, and (b) layer model depicting approximate composition of Ga(As)O and AlO layers. The modeling is with the depth resolution: 3 Å near surface and 8 Å at depth 40 Å.

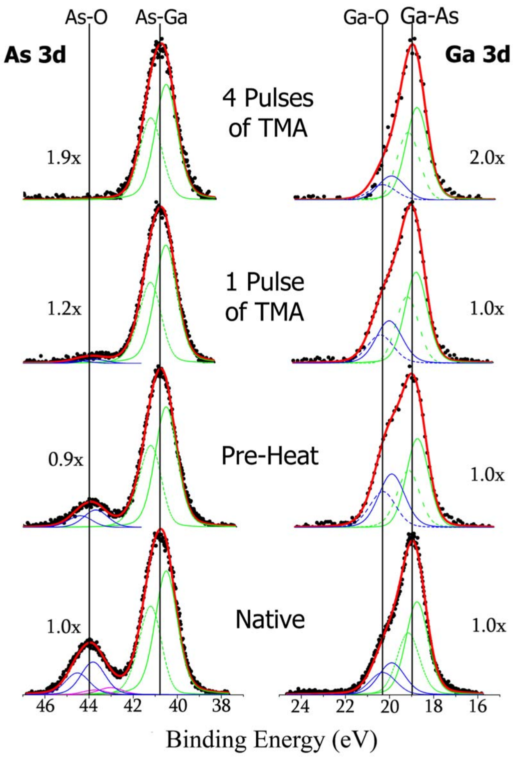

FIG. 2. (Color online) Comparison of the XPS spectra of the 3*d* peaks for Ga and As.

or surface hydroxyl groups. Without this additional O (0.5×10^{15} atom/cm^2) the stoichiometry of the Al oxide layer would be precisely 2:3. Therefore, ~65% of the oxygen (3×10^{15} atom/cm^2) in the native oxide layer move into the newly formed Al oxide layer, reducing the native oxide layer. After an additional three TMA pulses (also without any water exposure) the Al oxide thickness becomes 10 Å and there is a further slight decrease in the interfacial oxide.

The XPS results in Fig. 2 show the As 3*d* and Ga 3*d* core level spectra of native oxide, preheated (320 °C), after one TMA pulse, and after four TMA pulses (without any water exposure). Modeling of the native oxide spectrum indicates that there is a small amount of AsO (43.0 eV binding energy), but the majority consists of higher oxidation states attributed primarily to As_2O_3 (3*d* 5/2 at 43.8 eV); it is difficult to accurately differentiate (and quantify) As_2O_3 from As_2O_5 with our resolution. The sample heated to 320 °C exhibits a significant loss (gain) of the As (Ga) oxide signal. Interestingly, the relative amount of As_2O_3 loss (46%) is very close to the increase in Ga_2O_3 (47%). This is consistent with previous studies reporting the thermal conversion of mixed Ga/As oxides into predominantly Ga_2O_3.[11] However, the ambient exposure due to *ex situ* sample transfer precludes us from quantifying this further. The samples preheated to 320 °C for 30 min remain covered by an oxide consisting (according to XPS peak fittings) of a mixture of As_2O_3, As_2O_5, and Ga_2O_3. The Ga versus As ratio obtained from XPS is ~2:1, close to the ratio measured by MEIS, 2.3:1. After the initial TMA pulse, both the As 3*d* and Ga 3*d* core level intensities decrease, consistent with the existence of a partial AlO_x overlayer. More importantly, we see a significant decrease in the $As_2O_3+As_2O_5$ peak area (approximately 75%), whereas the decrease in the Ga_2O_3 peak is significantly less (~16%). An additional three TMA pulses (no water exposure) yields a further decrease in the AsO_x, and to a lesser extent Ga_2O_3, though the overall peak intensities do not change significantly. We conclude that the majority of the observed effects occur following the initial TMA pulse exposure, which is consistent with the "self-cleaning" mechanism proposed by previous studies.[12] Furthermore, it appears that AsO_x, when compared to GaO_x, more easily loses its oxygen to react with the Al from the TMA.[10,12]

Our observations on the "self-cleaning" effect by ALD reactions of TMA show quantitative results regarding the reduction of As oxides. Approximately 65% of native oxide including the majority (~75%) of the As oxides were reduced by the initial TMA pulse, as shown using both *in situ* MEIS and *ex situ* XPS. XPS also shows that several additional TMA pulses reduce all As oxides to a level below our detection limit, and the Ga oxides were also reduced substantially. In addition, the reaction mechanism for the TMA-native oxide system appears to be nonselective toward reducing the different As oxides (As_2O_3 and As_2O_5). However, this is not to suggest that prolonged TMA exposures can completely substitute surface chemical treatments; TMA would probably not remove surface hydrocarbons and other contaminants that can also have detrimental effects in devices (in fact, the term "self-cleaning" is perhaps misleading in this respect). However, our results do suggest that careful optimization of the TMA exposure (limiting the oxidant) during the initial few cycles of ALD growth could minimize the low quality interface oxide and increase the capacitance, improving overall device performance.

In conclusion, our MEIS and XPS studies show that the initial TMA pulse removes a majority (65%) of the native oxides and produces a 5 Å Al oxide layer. Introducing three additional TMA pulses to the same sample reduces all As oxides to below the XPS detection level and a substantial fraction of the Ga oxides obviating the need for a special etching treatment. Additional understanding of the mechanism behind this ALD reduction may be important for a range of potential III-V device applications.

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