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Letter

Native oxide consumption during the atomic layer deposition of TiO_2 films on GaAs (100) surfaces

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ABSTRACT

The consumption of the surface native oxides is studied during the atomic layer deposition of TiO_2 films on GaAs (100) surfaces. Films are deposited at 200 °C from tetrakis dimethyl amido titanium and H_2O. Transmission electron microscopy data show that the starting surface consists of ~2.6 nm of native oxide and X-ray photoelectron spectroscopy indicates a gradual reduction in the thickness of the oxide layer as the thickness of the TiO_2 film increases. Approximately 0.1–0.2 nm of arsenic and gallium suboxide is detected at the interface after 250 process cycles. For depositions on etched GaAs surfaces no interfacial oxidation is observed.

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1. Introduction

It's been well established that III–V semiconductors exhibit superior electrical properties compared to Si such as higher mobility and higher breakdown field. However, the absence of a high quality native oxide and observations of Fermi level pinning has discouraged their use in the microelectronics industry. [1] The introduction of high-k dielectrics has sparked renewed interest in III–V semiconductors, and recently there are several reports of good quality field effect transistors on GaAs combining the use of a high-k dielectric such as Al_2O_3 and HfO_2 with suitable predeposition surface preparation. [1–5] Additionally, several reports have been made of the existence of an interfacial cleaning mechanism that leads to the consumption of the surface native oxides during the atomic layer deposition (ALD) of the dielectric resulting in a practically sharp interface between the dielectric and semiconductor. [6–14] Similar ALD processes on hydrogen terminated Si surfaces have been known to result in the formation of SiO_2 based interfacial layers.[15] The main motivation for this work is to study the interface evolution during the ALD of TiO_2 on etched and native oxide GaAs surfaces. The precursor chosen belongs to the same amide family as the Hf precursors that have been shown to result in the consumption of the surface Ga and As oxides. A similar consumption reaction is observed for this ALD process indicating that the reaction byproducts may be responsible for these observations.

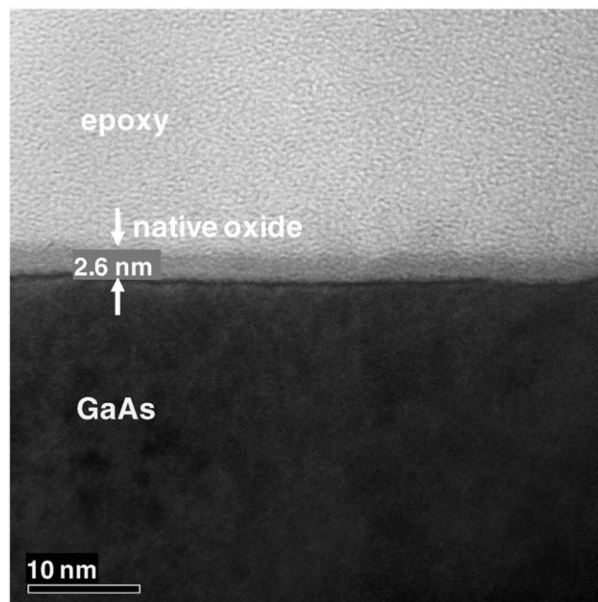

Fig. 1. Bright field TEM image of the starting native oxide covered GaAs (100) surface.

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2. Experimental details

The TiO_2 films were deposited in a homemade ALD reactor [16] from tetrakis dimethylamido titanium (TDMATi) and H_2O at 200 °C with 30 s purge times. GaAs (100) surfaces examined included cleaned native oxide surfaces as well as substrates etched in HF and NH_4OH solutions. [12] Ex-situ X-ray photoelectron spectroscopy (XPS) was used to examine the composition of the interface and performed with a Kratos AXIS 165 (Al achromatic X-ray source, 1486.6 eV), equipped with a hemispherical analyzer (165 mm radius). High resolution spectra of the As $2p_{3/2}$, As 3d, and Ga $2p_{3/2}$ regions were recorded at 0.1 eV step size, 20 eV pass energy, without charge neutralization, and with photoelectron emission normal to the sample surface. Some of the samples were sputter-thinned to permit recording of the Ga $2p_{3/2}$ and As $2p_{3/2}$ regions that are very surface sensitive. The high resolution spectra were baseline corrected and deconvolved using Lorentzian–Gaussian mixtures. The Lorentzian component was set at 40% for all peaks. In the As 3d region the substrate As $3d_{5/2}$ and $_{3/2}$ doublet was deconvolved by assuming functions of equal Full Width at Half Maximum (FWHM), a spin–orbit separation of 0.7 eV and intensity ratio of 3:2 and the substrate As $3d_{5/2}$ peak (As–Ga) was placed at a binding energy of 41.1 eV. The arsenic oxide contribution was estimated using separate peaks for As_2O_3 (chemical shift: +3.4 eV), As_2O_5 (+4.6 eV) and an arsenic suboxide metallic arsenic component AsO_x (+1.0 eV).[17,18] The As $2p_{3/2}$ region was similarly deconvoled using a peak for each of the three oxidation states described before (AsO_x: $+1.6\pm0.3$ eV, As_2O_3:+3.4 eV, As_2O_5: 4.7 eV) in addition to the substrate peak (1323.1 ± 0.1 eV).[10,19] This peak assignment produces a consistent oxide distribution between the As 3d and As $2p_{3/2}$ areas. In the Ga $2p_{3/2}$ region the spectra were fitted with peaks for the Ga_2O (chemical shift: $+1.0\pm0.1$ eV) and Ga_2O_3 ($+1.8\pm0.1$ eV) components in addition to the substrate peak ($1117.4\pm$ 0.1 eV) [17,19]. To maintain consistency the spectra in each region were fitted simultaneously. Charge compensation was performed using the As 3d and As $2p_{3/2}$ substrate peaks. Bright field transmission electron microscopy (TEM) and High Resolution TEM (HRTEM) data were provided by TEM ANALYSIS SERVICES LAB.

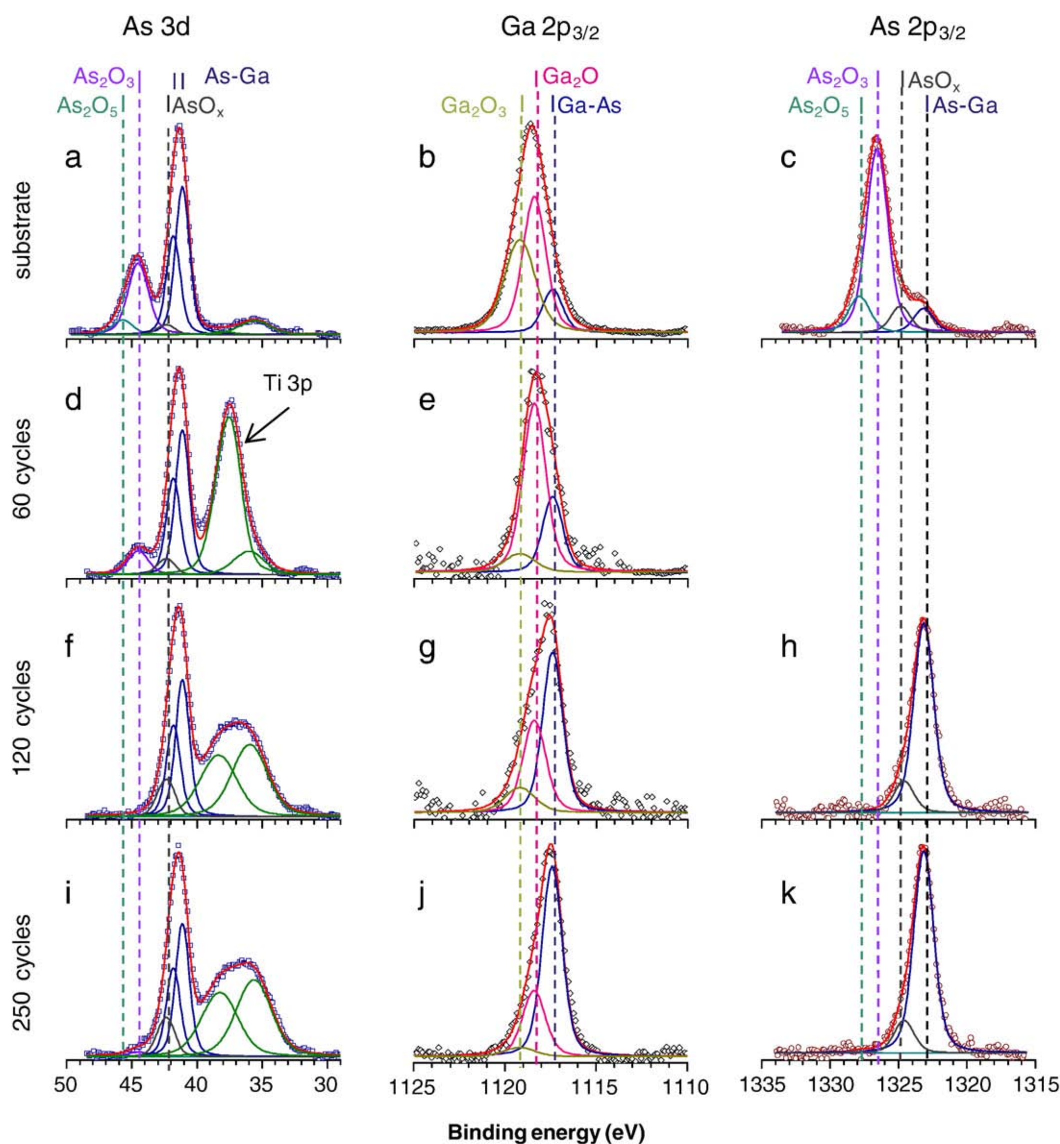

Fig. 2. As 3d, Ga $2p_{3/2}$ and As $2p_{3/2}$ high resolution XP spectra for the starting native oxide GaAs (100) surface (a–c), after 60 (d–e). 120 (f–h) and 250 (i–k) ALD cycles of TiO_2. The 120 and 250 cycle films have been sputtered in the XPS chamber to permit acquisition of the Ga $2p_{3/2}$ and As $2p_{3/2}$ spectral regions. The markers represent the experimental data and the overlaying solid line is the aggregate fit.

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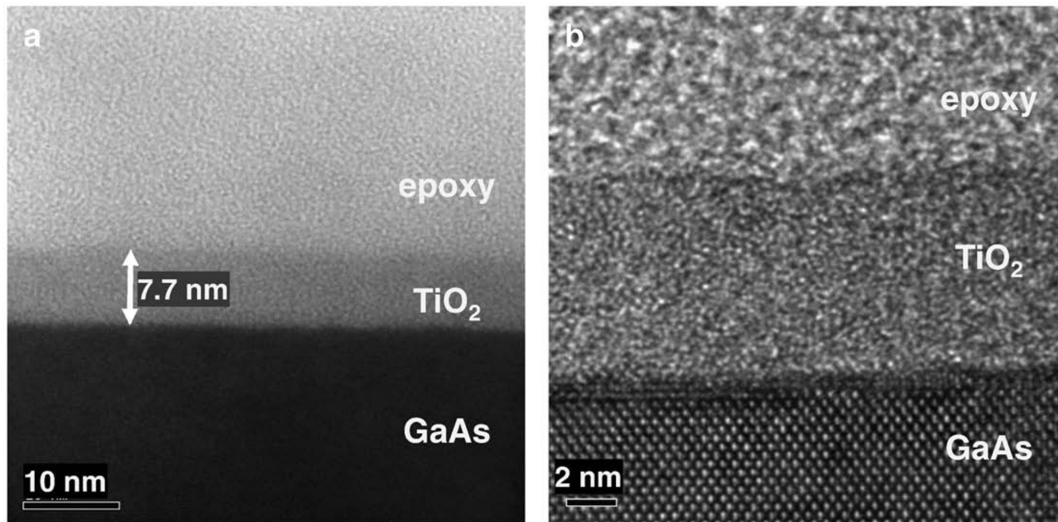

Fig. 3. Bright field (Fig. 3a) and HRTEM (Fig. 3b) data for a 120 ALD cycle film deposited on native oxide GaAs surface. The 7.7 nm film is smooth and homogeneous and no discernible interfacial layer can be seen corroborating the XPS results that suggest almost complete consumption of the starting ~2.5 nm native oxide layer during the deposition.

3. Results and Discussion

The process was optimized using films deposited on native oxide Si (100) substrates and the growth rate per cycle (GPC) vs. temperature plot indicated a practically constant GPC from 180 to 220 °C. As a result, all films examined in this work were deposited at 200 °C. Linear growth was confirmed both by spectroscopic ellipsometry (~0.06 nm/cycle) and Rutherford Back Scattering measurements (data not shown).

Bright field images for the starting cleaned native oxide GaAs surface show the presence of ~2.4–2.6 nm of native oxide (Fig. 1). Compositional analysis of like surfaces using XPS shows that the native oxide is Ga rich (As: 11% at.%, Ga: 23 at.%, and O: 66 at.%.). Fig. 2 shows the As 3d, Ga $2p_{3/2}$ and As $2p_{3/2}$ XP spectra for (a) the starting native oxide surface, (b) after 60 ALD cycles, (c) after 120 ALD cycles and (d) after 250 ALD cycles. The As $2p_{3/2}$ region is not visible for the 60 cycle film because the film thickness is large compared to the electron mean free path ($\lambda = 0.67$ nm).[20] The 120 and 250 cycle films were sputter-thinned in the analytical chamber to permit probing of the Ga $2p_{3/2}$ and As $2p_{3/2}$ regions. However, as shown by the strong Ti 3p signal in the As 3d region enough of the TiO_2 film was left to protect the integrity of the interface. While the absolute intensity for any substrate peak is attenuated by the presence of the TiO_2 film, the exponential attenuation of the signal leaves the ratio of the oxide to the corresponding substrate peak independent of the overlayer thickness. As a result, this ratio is suitable to track any changes to the native oxide thickness. If the native oxide thickness remains unchanged during the deposition then the ratio of the oxide to the substrate peak will remain constant regardless

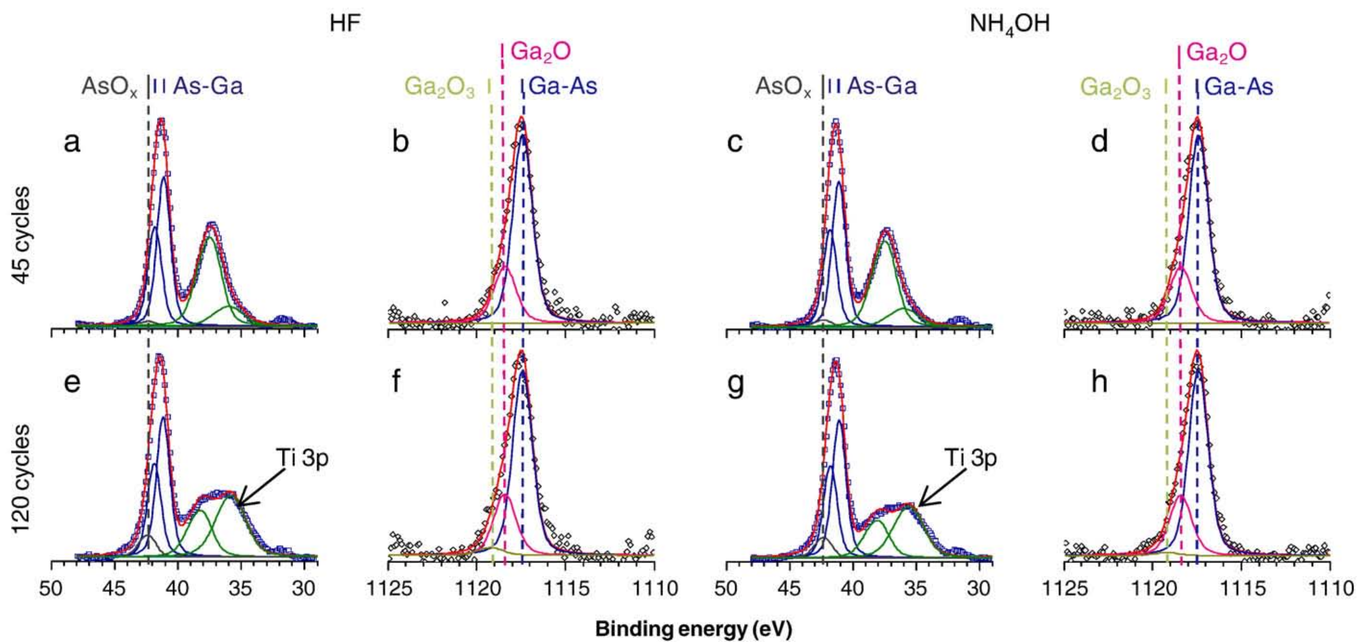

Fig. 4. As 3d (a, c, e, g), and Ga $2p_{3/2}$ (b, d, f, h) high resolution XP spectra for 45 (a, b, c, d) and 120 (e, f, g, h) cycle films deposited on HF (a, b, e, f) and NH_4OH (c, d, g, h) etched GaAs (100) surfaces. The 120 cycle films have been sputtered in the XPS chamber to permit acquisition of the Ga $2p_{3/2}$ spectra. The markers represent the experimental data and the overlaying solid line is the aggregate fit.

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of the thickness of the overlayer. If the native oxide is thinned during the deposition then a decrease in the ratio will be observed. This is indeed the case for both the As and Ga interfacial oxides. As can be seen in Fig. 2 there is substantial reduction in the oxide/substrate ratio for the As 3d region after 60 process cycles and practically zero oxide intensity is observed after either 120 or 250 ALD cycles. For the 120 and 250 cycle films an increase in the concentration of arsenic suboxide/metallic arsenic is observed. These results are mirrored in the As $2p_{3/2}$ region. For the Ga $2p_{3/2}$ region the reduction in the oxide intensity is not as easily observed due to the overlap of the substrate and oxide peaks. However, the peak deconvolution and peak shape change both indicate a gradual consumption of the gallium oxides. The FWHM is decreasing gradually with cycle number and the peak shape changes from practically symmetric for the starting surface to displaying a high binding energy tail for the 120 and 250 cycle samples. The FWHM of the peak for the 250 cycle film is smaller than that for the 120 cycle film indicating that the etching reaction continues to consume the interfacial Ga_2O even after 120 process cycles. It appears that the higher binding energy Ga_2O_3 is consumed faster while the Ga_2O persists at the interface with a small concentration equivalent to ~0.1 nm detected after 250 process cycles.

Bright field TEM and HRTEM data for a piece of the same 120 cycle film is shown on Fig. 3. Both images show the presence of an amorphous, homogeneous and smooth film on the GaAs surface. There is no discernible contrast or interface present in the images corroborating the XPS results that suggest the consumption of almost all the starting native oxide layer.

Fig. 4 shows As 3d and $Ga2p_{3/2}$ XP spectra for 45 and 120 cycle films deposited on GaAs etched in either HF or NH_4OH solutions. The 120 cycle films were sputter-thinned in the analytical chamber. The spectra are pretty similar for all four samples and show less interfacial AsO_x than the films deposited on native oxide. The Ga $2p_{3/2}$ spectra are very similar to that obtained for the 250 cycle film on the native oxide starting surface. It appears that the last 0.1–0.2 nm of interfacial Ga_2O is very hard to remove even when the starting surface is etched. However, since the presence of Ga_2O at the interface has been shown not to cause Fermi level pinning it may not be affect the electrical properties of the stack significantly [21–23].

4. Conclusions

The native oxides of the GaAs surface are gradually consumed during the ALD of TiO_2 from TDMATi and H_2O at 200 °C. The arsenic oxides are consumed faster leaving behind ~0.1 nm of arsenic suboxide/metallic arsenic. The consumption of the gallium oxides is slower but persists even after 120 ALD cycles. Approximately 0.1 nm of Ga_2O remains at the interface regardless of the surface preparation.

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