Indium stability on InGaAs during atomic H surface cleaning

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Atomic H exposure of a GaAs surface at 390 °C is a relatively simple method for removing the native oxides without altering the surface stoichiometry. *In-situ* reflection high energy electron diffraction and angle-resolved x-ray photoelectron spectroscopy have been used to show that this procedure applied to $In_{0.2}Ga_{0.8}As$ effectively removes the native oxides resulting in an atomically clean surface. However, the bulk InGaAs stoichiometry is not preserved from this treatment. The In:Ga ratio from the substrate is found to decrease by 33%. The implications for high-mobility channel applications are discussed as the carrier mobility increases nearly linearly with the In content. © *2008 American Institute of Physics*. [DOI: 10.1063/1.2919047]

One of the approaches being considered for future complementary metal-oxide-semiconductor devices is the substitution of silicon with high-mobility channels, where $In_xGa_{1-x}As$ is one of the preferred candidates for metal-oxide-semiconductor field-effect transistor (MOSFET) applications.[1] However, the interface thermal stability and interface quality of oxide insulators on InGaAs and other III-V semiconductors are far more complex than those on Si. Having more than one substrate element reacting with the oxide at the interface with different formation and decomposition energetics will lead to reaction channels resulting in various desorption and segregation products.[2] To preserve a stoichiometric InGaAs surface, one of the reported solutions employs an As-capping layer that is desorbed at relatively low temperatures[3,4] prior to further deposition. However, some methods for epitaxial growth of InGaAs on GaAs such as metal-organic chemical vapor deposition are not feasible with As capping.[5] An alternative to As capping includes passivation using the surface oxides which can be removed upon hydrogen plasma treatment (HPT) at a substrate temperature below 250 °C, where it has been reported that no detectable surface decomposition occurs by x-ray photoelectron spectroscopy (XPS).[3,5] Atomic hydrogen treatment (AHT) from a H_2 thermal cracking source is an alternative technique for the removal of the oxide capping layer being advantageous over HPT as no H ions are supplied. This letter describes the reaction channels observed during the removal of air exposed grown native oxide on (13.5 nm) $In_{0.2}Ga_{0.8}As$/GaAs(001) upon AHT at 390 °C and subsequent *in-situ* reflection high energy electron diffraction (RHEED) and XPS analysis. It is found that the AHT procedure results in an atomically clean (2×4 reconstructed) $In_xGa_{1-x}As$ surface. However, an indium depletion at the surface and subsurface regions is detected which may be expected to impact performance such as interface defect state densities and channel mobility in MOSFET devices.[6,7]

The sample employed for this study was a commercial (13.5 nm) $In_{0.2}Ga_{0.8}As$ layer grown by molecular beam epitaxy[8] on a semi-insulating GaAs(001) wafer with a GaAs

buffer layer of 535 nm thick. The $In_{0.2}Ga_{0.8}As$ layer and GaAs buffer layer were doped each with Si (*n* type, 1×10^{17} cm^{-3}). The $In_{0.2}Ga_{0.8}As$/GaAs wafer was in a sealed container for several weeks. The container was opened and the wafer was immediately loaded into an ultrahigh vacuum (UHV) process chamber equipped with an atomic hydrogen source,[9] RHEED gun, and substrate heating capability.[10] The base pressure in the process chamber is better than 5×10^{-10} mbar and is connected through UHV with an XPS system described elsewhere.[11] The sample was heated to 390 °C for 30 min and then exposed to atomic hydrogen for up to 30 min with a background pressure of 1×10^{-6} mbar (corresponding to 1.35 kL of H exposure, where 1 L≡1 $\times 10^{-6}$ torr s). After the 30 min AHT, an additional H exposure was carried out for 120 min (a total of 5.4 kL H exposure). Previous reports showed that these experimental conditions for the atomic H cleaning on GaAs produce an atomically clean surface free of oxides.[12–14] The RHEED pattern was captured at 30 kV with an incident angle of $1-2°$. The XPS data were recorded at intermediate steps in the sample preparation process using an Al $K\alpha_1$ monochromatic source and a hemispherical analyzer.[15] XPS spectra were taken at 45° (surface sensitive) and 75° (bulk sensitive) take-off angles measured with respect to the surface plane. XPS spectra fits were performed by using the software AANALYZER (Ref. 16) using fixed values for parameters such as Lorentzian/Gaussian ratios, spin-orbit splitting, and branching ratios, which are either known or directly determined from the atomically clean InGaAs substrate.

Figure 1 shows the Ga 3d and In 4d XPS regions for the InGaAs surface with (a) the native oxides, and (b) after a 30 min annealing at 390 °C plus 150 min of AHT at the same temperature. The XPS data for 45° and 75° take-off angles are normalized to visually compare the intensity ratio of the In:Ga signals at the different probing depths. The In 4d signal from the substrate shows resolvable doublet features 4$d_{5/2}$ and 4$d_{3/2}$ at 17.58 and 18.42 eV, respectively. The In 4$d_{5/2}$ feature from the In_2O_3 (In^{3+} oxidation state) appears at 18.51 eV overlapping with the In 4$d_{3/2}$ from the substrate. The Ga 3$d_{5/2}$ and 3$d_{3/2}$ from the substrate appear at 19.37 and 19.83 eV, respectively, while the Ga 3$d_{5/2}$ from the Ga_2O_3 (Ga^{3+}) is at 20.48 eV.

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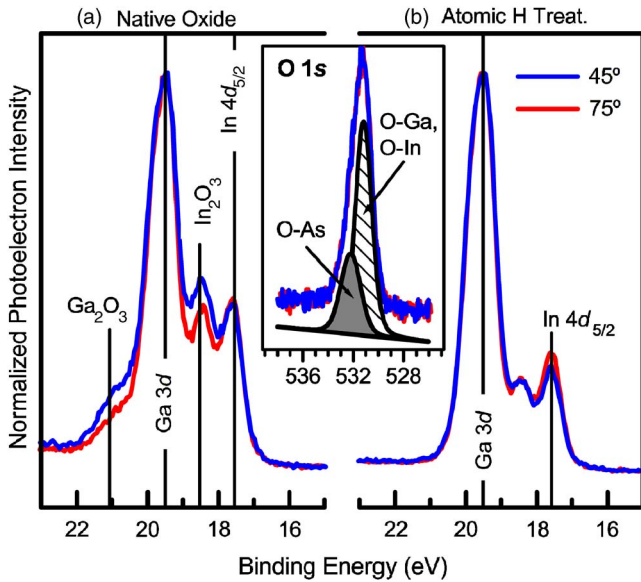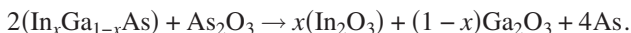b)Electronic mail: rmwallace@utdallas.edu.

FIG. 1. (Color online) Normalized XPS spectra for 45° and 75° take-off angles for Ga 3d and In 4d core levels for (a) InGaAs native oxide and (b) after 30 min annealing plus an atomic H treatment at 390 °C for 150 min. The inset shows the normalized O 1s XPS component from the native oxide for 45° and 75° take-off angles. The O 1s component at 532.19 eV belongs to O–As bonds while the component at 531.16 eV belongs to the O–Ga and O–In bonds.

FIG. 2. (Color online) XPS spectra peak fits of (a) Ga 3d, In 4d, and (b) As 3d regions for native oxide (bottom), plus 30 min annealing in UHV (middle bottom), plus 30 min of AHT at 390 °C, (middle top) and plus 120 min of AHT at 390 °C (top). (a) Bottom and top plots correspond to the 45° take-off data shown in Fig. 1. The broad shaded features in (a) are associated with Ga and In oxides. As 3d from the InGaAs native oxide shows As^{5+} and As^{3+} chemical components associated with As$_2$O$_5$ and As$_2$O$_3$, respectively.

The In:Ga signal ratio from the bulk sample with a native oxide does not depend on the take-off angle, as confirmed in Fig. 1(a). This observation suggests a uniform composition of such elements (for Ga 3d and In 4d core levels) through the sampling depth of the InGaAs crystal ($\sim$7.5 nm). We note that the XPS intensity ratio In/Ga is larger in the oxide layer (In/Ga=1.07) than in the bulk (In/Ga=0.55). In addition, the O 1s signal (inset of Fig. 1) does not show any angular dependence which agrees with a homogeneous oxide distribution, consequently the group III native oxide is In rich. Figure 1(b) shows that after the AHT at 390 °C for 150 min, the In:Ga ratio in the InGaAs layer drops by 52% and that there is a dependence on the take-off angle of the In:Ga ratio, which translates into an In concentration decrease at the surface.

To further explore the reaction channels leading to indium concentration reduction in the surface region, XPS spectra for In, Ga, and As taken at intermediate steps in the sample preparation process are shown in Fig. 2. The native oxide shows the presence of Ga$_2$O$_3$, In$_2$O$_3$, As$_2$O$_3$, and elemental As (As–As bonds), as predicted by the equilibrium phase diagram for the quaternary In–Ga–As–O.[17] As$_2$O$_5$ is also present in the native oxide. After 30 min annealing in UHV at 390 °C, the As oxides disappear and As^0 and In$_2$O$_3$ are dramatically reduced to a level near the detection limit while the Ga$_2$O$_3$ feature intensity significantly increases. This can be roughly explained with the following reaction path accompanied with As$_2$O$_5$, As^0, and In$_2$O$_3$ thermal desorption at 390 °C:[18]

$$2(\text{In}_x\text{Ga}_{1-x}\text{As}) + \text{As}_2\text{O}_3 \rightarrow x(\text{In}_2\text{O}_3) + (1-x)\text{Ga}_2\text{O}_3 + 4\text{As}.$$

After 30 min of AHT at 390 °C, all remaining oxides and elemental As disappear (below the detection limit of XPS $\sim$0.1%) as well as any associated O 1s signal (not shown). The reaction paths for Ga oxide decomposition upon the exposure o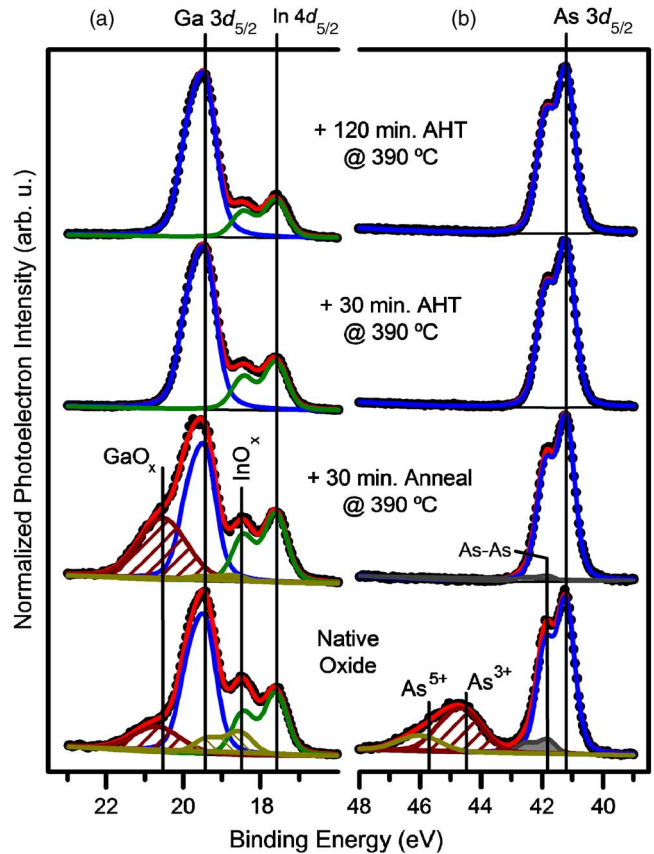f atomic hydrogen from GaAs native oxide have been discussed by Yamada *et al.*[19,20] They suggest a two step reaction; first a temperature independent reaction with H followed by a thermally activated desorption of volatile products. We assume a similar mechanism for In oxide. The possible reaction paths for Ga and In oxides removal are as follows:

$$\text{Ga}_2\text{O}_3 + 4\text{H} \rightarrow (\text{Ga}_2\text{O}\uparrow + 2\text{H}_2\text{O}\uparrow) \quad \text{and} \quad (2\text{GaOH}\uparrow + \text{H}_2\text{O}\uparrow),$$

$$\text{In}_2\text{O}_3 + 4\text{H} \rightarrow (\text{In}_2\text{O}\uparrow + 2\text{H}_2\text{O}\uparrow) \quad \text{and} \quad (2\text{InOH}\uparrow + \text{H}_2\text{O}\uparrow).$$

In addition to the surface oxide species removal,[21] it is also noted that the In:Ga ratio in the near-surface In$_{1-x}$Ga$_x$As layer has dropped about 33% with respect to the initial surface. An additional 120 min of AHT at 390 °C results in further reduction of the In:Ga ratio (52% drop).

Figure 3(a) shows the In:Ga, In:As, and Ga:As XPS intensity ratios in the In$_{1-x}$Ga$_x$As layer for the several intermediate steps. Solid and open symbols correspond to the data taken at take-off angles of θ=45° and 75°, respectively, and the error bars are within the size of the data symbols. The In:As ratio remains nearly constant after the UHV annealing step while the In:Ga ratio increases. The In:Ga ratio increase occurs with the In being segregated at the surface over the Ga (larger ratio at 45° take-off angle). Conversely, the Ga:As ratio decreases to the same extent that the In:Ga ratio increases. These observations are consistent with a Ga concen-
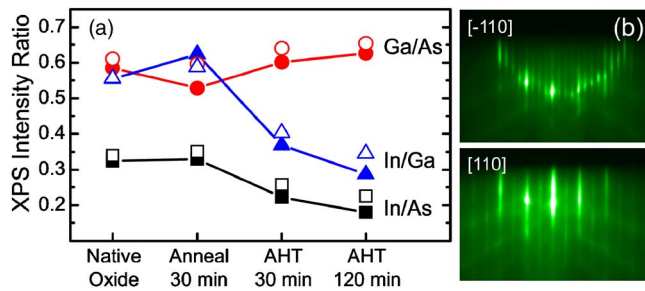
FIG. 3. (Color online) (a) XPS intensity ratios for In 4d, Ga 3d, and As 3d species in the InGaAs substrate for the several steps indicated in Fig. 2. Even though the XPS intensity ratios are not normalized with the atomic sensitivity factors, the trend of these ratios are closely related to the atomic concentration changes in the sample. The intensity ratio error bars that include the experimental and analysis errors are less than ± 0.01 and are within the size of the data symbols in this plot. (b) RHEED patterns of azimuths [-110] and [110] showing a sharp (2×4) surface reconstruction (As rich) after 30 min of AHT at 390 °C. Solid symbols: $\theta = 45°$; open symbols: $\theta = 75°$.

tration reduction near the surface with respect to In and As. The conservation of the In:As ratio is likely due to the overlying Ga_2O_3 capping layer. Prolonged anneals at 390 °C in UHV (no AHT) up to 180 min performed on a separate sample (control sample) showed small variations in substrate elemental compositions and a small reduction in surface Ga_2O_3. Note that the data points in Fig. 3 are the ratios of the areas from the deconvolution of the data shown in Fig. 2 and not the ratios of atomic concentrations which will require the normalization with carefully calibrated atomic sensitivity factors not available in the present study.

After the initial and subsequent AHT, the In:Ga ratio substantially decreases showing an In concentration reduction relative to Ga. The In:Ga ratio is larger at 75° takeoff indicating that In concentration is even smaller at the surface. Ga:As and In:As ratios are consistently smaller at 45° takeoff throughout all the steps. It is clear that the InGaAs substrate surface is As rich even after prolonged AHT indicating the segregation of As at the surface region. We note that, from temperature programed desorption studies on $In_{0.22}Ga_{0.78}As/GaAs$,[22] desorption of In from the surface (bulk) appears to occur at 620 °C (700 °C). In contrast, we observe a further drop in indium surface concentration at 390 °C only after the complete removal of detectable native oxides with the exposure to atomic H. Moreover, additional In loss from the bulk $In_{1-x}Ga_xAs$ due to prolonged AHT is also observed. We speculate that the apparently enhanced desorption mechanism leading to a lower In desorption temperature may be due to the formation of InH_x compounds.[21,23]

Despite the loss of In at the surface after AHT, the procedure provides an atomically clean (2×4) reconstructed surface. Figure 3(b) shows the RHEED patterns along the [-110] and [110] azimuths for the 30 min AHT step. A sharp (2×4) surface reconstruction is observed which is a confirmation of As-dimer formation (As-rich or As-terminated surface).[24,25] This is in agreement with the angular dependence of the Ga:As and In:As ratios showing an As-rich surface.

In summary, the stability of $In_{0.2}Ga_{0.8}As$ and its native oxide upon anneals at 390 °C and the effects of atomic hydrogen exposure have been discussed. From angle resolved XPS (ARXPS), it was found that the InGaAs native oxide consisted mainly of Ga_2O_3, In_2O_3, and As_2O_3, which are uniformly distributed through the oxide layer. ARXPS analysis after annealing and exposure to atomic hydrogen indicates a marked In:Ga ratio decrease in the subsurface region with further In depletion at the surface. The implication of the observed In concentration gradient on electronic properties of InGaAs with respect to GaAs is important in regards to MOSFET applications. It seems clear that process temperatures for MOSFET fabrication processes with a significant hydrogen ambient must be kept below 390 °C to avoid such concentration gradients and the potential reduction of carrier mobility.

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