Arsenic decapping and half cycle reactions during atomic layer deposition of \( \text{Al}_2\text{O}_3 \) on \( \text{In}_{0.53}\text{Ga}_{0.47}\text{As}(001) \)

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In situ x-ray photoelectron spectroscopy was performed during thermal desorption of a protective As layer and subsequent atomic layer deposition (ALD) of \( \text{Al}_2\text{O}_3 \) on \( \text{In}_{0.53}\text{Ga}_{0.47}\text{As}(001) \). \( \text{H}_2\text{O} \) dosing on the As-decapped surface caused formation of As oxides and As hydroxides, which were reduced by a subsequent trimethylaluminum (TMA) pulse. However, when a TMA pulse was performed first, the \( \text{In}_{0.53}\text{Ga}_{0.47}\text{As}(001) \) surface did not oxidize during subsequent ALD cycles, suggesting passivation by TMA adsorption at water-reactive sites. Scanning tunneling microscopy performed on a structurally-similar \( \text{InAs}(001) \) surface after \( \text{H}_2\text{O} \) dosing revealed that surface defects are created by displacement of surface As atoms during oxidation. These surface defects act as interface states, consistent with the inferior capacitance-voltage characteristics of \( \text{H}_2\text{O} \)-first ALD-\( \text{Al}_2\text{O}_3 \) capacitors compared to TMA-first samples. © 2010 American Institute of Physics. [doi:10.1063/1.3452336]

Continued scaling of the feature size of metal-oxide-semiconductor (MOS) devices stimulates efforts to introduce both high-\( k \) dielectric gate insulators and high mobility channel materials such as \( \text{In}_x\text{Ga}_{1-x}\text{As} \).1 Atomic layer deposition (ALD) has been the technique of choice for the deposition of high-\( k \) dielectric films in most recent studies. The reaction chemistry between ALD precursors and the semiconductor or oxide surface dictates the quality of both the high-\( k \)/semiconductor interface and the bulk of the high-\( k \) film.2,3 Therefore, it is of great interest to investigate the evolution of the chemical state of the interface during ALD. Recently, MOS capacitors consisting of ALD-\( \text{Al}_2\text{O}_3 \) and an n-\( \text{In}_{0.53}\text{Ga}_{0.47}\text{As}(001) \) channel layer, whose protective As capping layer was thermally removed in the ALD reactor prior to \( \text{Al}_2\text{O}_3 \) deposition, have been shown to exhibit superior electrical characteristics compared to \( \text{Al}_2\text{O}_3 \) deposited on an initially native oxide-coated \( \text{In}_{0.53}\text{Ga}_{0.47}\text{As} \).4

In this paper, in situ x-ray photoelectron spectroscopy (XPS) results are reported that probe both the thermal desorption of a protective As capping layer from an \( \text{In}_{0.53}\text{Ga}_{0.47}\text{As}(001) \) surface and subsequent half cycle reactions of ALD-\( \text{Al}_2\text{O}_3 \) on the decapped surface. In addition, atomic-scale effects of \( \text{H}_2\text{O} \) dosing of a clean \( \text{InAs}(001) \) surface, which is structurally similar to \( \text{In}_{0.53}\text{Ga}_{0.47}\text{As}(001) \), are reported using scanning tunneling microscopy (STM).

The ALD reactor used in this study is equipped with a differentially pumped in situ XPS system, details of which can be found elsewhere.5 To avoid possible charging of the sample surface during XPS measurements, the sample holder (a 4 inch Si wafer) was coated with Au. An exposed area of the Au coating, i.e., the area that was not covered by an \( \text{In}_{0.53}\text{Ga}_{0.47}\text{As} \) sample, was also used for calibrating XPS binding energies. The starting sample consists of an approximately 50 nm thick protective As capping layer and a 200 nm thick \( \text{In}_{0.53}\text{Ga}_{0.47}\text{As} \) channel layer grown on an InP substrate. The As capping layer was thermally desorbed at 380 °C under high vacuum. The completion of As decapping was confirmed by the chemical shift in As 3d peaks by \( \sim-0.8 \) eV as well as by the change in the background pressure. Following decapping, ALD-\( \text{Al}_2\text{O}_3 \) was carried out at 270 °C, using trimethylaluminum (TMA) and water vapor with TMA being the first pulse. In another experiment, multiple doses of \( \text{H}_2\text{O} \) were injected before starting TMA-first \( \text{Al}_2\text{O}_3 \) deposition. After each half cycle, the reactor was pumped down to \( \sim10^{-6} \) Torr momentarily while in situ XPS was performed.

In our previous study,4 a native-oxide free and atomically abrupt interface between an \( \text{Al}_2\text{O}_3 \) layer grown by ALD...
(with TMA pulse being the first) and As decapped In$_{0.53}$Ga$_{0.47}$As(001) was observed. The typical growth rate of ALD-Al$_2$O$_3$ is less than one monolayer per cycle,$^6$ and therefore, during the first few cycles of the ALD, a portion of the decapped In$_{0.53}$Ga$_{0.47}$As surface was exposed to H$_2$O pulses and the background residual moisture present in an ALD system that uses H$_2$O as an oxidant.$^6$ The absence of detectable group III and group V oxides at the intensity of tails on the higher binding energy side normalized by the maximum intensity of each spectrum. The subsequent TMA pulse. The As spectra are smoothed and eV of the decapped In$_{0.53}$Ga$_{0.47}$As surface was exposed to H$_2$O pulses and the background residual moisture present, therefore, during the first few cycles of the ALD, a portion for the TMA and H$_2$O/TMA dosed surfaces. Note that both (a) and (b) are drawn on the same vertical scale, and the difference shown in (b) is magnified by ten times.

To test the first scenario, multiple pulses of H$_2$O were deliberately dosed prior to TMA dosing and the surface was monitored with in situ XPS. The inset of Fig. 1 presents As 3$d$ spectra taken after the decapping, after five initial pulses of H$_2$O dosing (referred to as pre-H$_2$O), and after a subsequent TMA pulse. The As spectra are smoothed and normalized by the maximum intensity of each spectrum. The intensity of tails on the higher binding energy side (43–46 eV) increased after the pre-H$_2$O dosing, indicating the formation of a component containing As whose oxidation state is higher than that of As in the InGaAs substrate. To identify the chemical state of this higher binding energy component, the As 3$d$ spectrum after the pre-H$_2$O dosing was deconvoluted into two peaks; the peak at lower binding energy has the same binding energy and full width at half maximum as the As 3$d$ feature after decapping, and therefore, originates from the InGaAs substrate. The peak separation between the new component and the As 3$d$ of the InGaAs is ~3 eV, similar to the reported chemical shift in As$_2$O$_3$.$^9$ However, as discussed below, there may be contributions to the higher binding energy peak from suboxides or hydroxyl species, AsO$_x$H$_y$. The subsequent TMA pulse (1st TMA) reduced the intensity of the higher binding energy tail, suggesting the reduction in AsO$_x$/AsO$_2$H$_y$ during the TMA pulse. With regard to the In 3$d$ spectra (not shown), the comparison of the In 3$d$ features before and after the H$_2$O dosing are essentially identical, indicating that the H$_2$O dosing was not capable of forming an In oxide stable at the 270 °C ALD temperature.

In contrast to H$_2$O-first dosing, when a freshly decapped surface was treated with a TMA pulse first, the shape of As 3$d$ feature (after normalization of its absolute intensity) remained unchanged; see Fig. 2. This is shown in detail by plotting the difference in XPS As 3$d$ spectra relative to the decapped sample for the TMA and H$_2$O/TMA dosed surfaces; the difference is less than the noise level of the spectra. Based on the observation that the decapped In$_{0.53}$Ga$_{0.47}$As surface was susceptible to oxidation by H$_2$O pulses, while the decapped surface treated with the initial TMA pulse remained unaltered upon a pulse of H$_2$O, proposed model (ii) [strong resistance of the decapped to oxidation by H$_2$O(g) after initial TMA dosing] is favored. On the decapped In$_{0.53}$Ga$_{0.47}$As surface, there may exist preferred sites for oxidation by H$_2$O, and a single pulse of TMA—although it is not sufficient to entirely saturate all of the potential bonding sites on the surface—can effectively passivate these water reactive sites, because they have the highest binding energy for adsorbates, preventing their reaction with H$_2$O.

Even though TMA dosing reduces As oxide/hydroxide formed by initial H$_2$O exposure, the sequence of ALD precursors introduced (i.e., TMA-first versus H$_2$O-first) is still critical, as illustrated in Fig. 3. H$_2$O-first ALD-Al$_2$O$_3$ capacitors exhibit inferior capacitance-voltage (CV) characteristics compared to TMA-first samples; a more stretched-out CV curve is measured across the measured gate bias range, indicating a higher density of interface traps for the H$_2$O-first sample compared to the TMA-first sample.$^{10}$

A major concern with the H$_2$O-first ALD process is the displacement of surface As atoms, as revealed by STM of group III rich surface, InAs(001)-(4×2). InAs(001)-(4×2) is employed instead of In$_{0.53}$Ga$_{0.47}$As(001)-(4×2) because the former has a much lower defect density, thereby making STM imaging and adsorbate site assignment easier. The (4×2) surface reconstructions of each semiconductor are almost identical.$^{11}$ The InAs surface was exposed to HPLC-grade H$_2$O vapor at 10–100 mTorr and 25 °C for 1 to 2 min,
and the samples were subsequently annealed in UHV. Note that the ALD experiments were performed with 270 °C H₂O dosing, which may produce slightly different As oxides. The clean InAs(001)-(4×2) surface consists of rows and trough features oriented in the [110] direction. After annealing the H₂O dosed surface at 200 °C, the H₂O induced reaction sites appear in the trough regions [Fig. 4(a)]. The H₂O-exposed, 350 °C-annealed InAs(001)-(4×2) surface has dark cuts in the rows that are not present on the clean surface [green boxes in Fig. 4(b)] consistent with As atom displacement. Additionally, new, ordered regrowth is seen nucleating at the step edges and forming zig-zag rows in the [−110] direction [arrow in Fig. 4(b)]. These regions of regrowth are identical to the (2×4) surfaces of InAs(001) and InGaAs(001), known as the α2(2×4) reconstruction. Due to the presence of these surface As vacancy cuts in the rows and the α2(2×4) reconstruction, it is likely that As atoms are displaced by the reaction of the InAs substrate with H₂O and diffuse on the surface to form areas of α2(2×4) regrowth upon annealing.

To prove that these are just displaced As atoms and that no oxygen remains on the surface, a 450 °C anneal was performed. This anneal restored the original (4×2) reconstruction with no additional defect sites. The results are consistent with no loss of As to the gas phase, i.e., the chemisorption of water is reversible. Given the structural similarity between an InAs(001) and an In₀.₅₅Ga₀.₄₇As(001) surface, it is expected that the H₂O dosing on the decapped In₀.₅₅Ga₀.₄₇As(001) would also have caused the displacement of As atoms forming As–As bonds at 350 °C and complete restoration of the clean surface at 450 °C, as in the case of the InAs(001) surface. Restoration of the clean InAs(001)-(4×2) surface via high temperature annealing was observed for all doses of H₂O.

The XPS results show that after H₂O dosing, at 270 °C, there are likely As–O and/or As–OH bonds on surface, and the STM results show that at 350 °C there is only As₂ on the surface, while at 450 °C in UHV the clean III-V surface is restored. This suggests that in the UHV environment of STM, most of the arsenic oxides/hydroxides decompose via a pathway similar to: H₂O(g) + InGaAs(001)-(4×2) → AsO₃Hₓ/InGaAs(001)-(4×2) → As₂/InGaAs(001)-(4×2) + H₂O(g) → InGaAs(001)-(4×2). Although a subsequent TMA pulse at modest temperature (270 °C) is also capable of reducing AsO₃Hₓ formed by the initial H₂O pulse on a decapped InGaAs surface, it is unlikely that displaced As atoms will be restored to their original surface sites at 270 °C. Displaced As surface atoms produce dangling bonds on Group III surface atoms and residual As–As bonds. Because of the modest energy resolution of the nonmonochromatic in situ XPS apparatus, the As–As bonds cannot be distinguished from the bulk As in InGaAs. However, both the dangling bonds and the displaced As atoms created by H₂O dosing are expected to provide electrically active interface states in MOS devices, consistent with the CV results shown in Fig. 3.

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6At our ALD temperature, 270 °C, desorption of chemisorbed precursors from the surface is negligible, as confirmed by an identical XPS spectrum collected after several hours since the initial scan.
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