Arsenic decapping and half cycle reactions during atomic layer deposition of Al_2O_3 on $In_{0.53}Ga_{0.47}As(001)$

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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 Al_2O_3 on $In_{0.53}Ga_{0.47}As(001)$. H_2O 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 $In_{0.53}Ga_{0.47}As(001)$ 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 InAs(001) surface after H_2O 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 H_2O-first ALD-Al_2O_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 $In_xGa_{1-x}As$.[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-Al_2O_3 and an n-$In_{0.53}Ga_{0.47}As(001)$ channel layer, whose protective As capping layer was thermally removed in the ALD reactor prior to Al_2O_3 deposition, have been shown to exhibit superior electrical characteristics compared to Al_2O_3 deposited on an initially native oxide-coated $In_{0.53}Ga_{0.47}As$.[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 $In_{0.53}Ga_{0.47}As(001)$ surface and subsequent half cycle reactions of ALD-Al_2O_3 on the decapped surface. In addition, atomic-scale effects of H_2O dosing of a clean InAs(001) surface, which is structurally similar to $In_{0.53}Ga_{0.47}As(001)$, 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 $In_{0.53}Ga_{0.47}As$ sample, was also used for calibarting XPS binding energies. The starting sample consists of an approximately 50 nm thick protective As capping layer and a 200 nm thick $In_{0.53}Ga_{0.47}As$ 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 3*d* peaks by ~−0.8 eV as well as by the change in the background pressure. Following decapping, ALD-Al_2O_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 H_2O were injected before starting TMA-first Al_2O_3 deposition. After each half cycle, the reactor was pumped down to $\sim 10^{-6}$ Torr momentarily while *in situ* XPS was performed.

In our previous study,[4] a native-oxide free and atomically abrupt interface between an Al_2O_3 layer grown by ALD

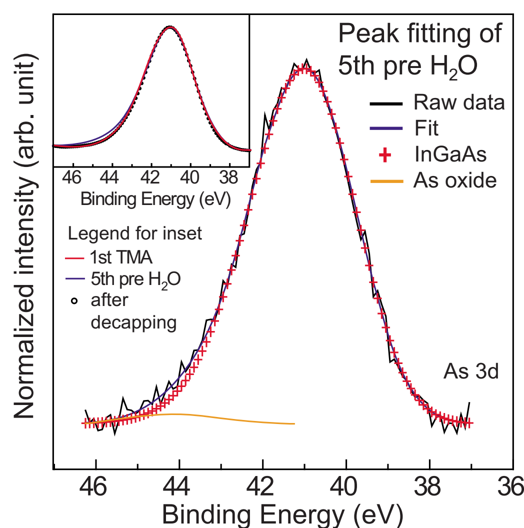

FIG. 1. (Color online) Deconvolution of As 3*d* peak after 5th pre-H_2O which illustrates the formation of AsO_x after the H_2O dosing. Smoothed and normalized (by the maximum intensity) As 3*d* core level XPS spectra taken after decapping, 5th pre-H_2O pulse, and a subsequent TMA pulse are shown in the inset.

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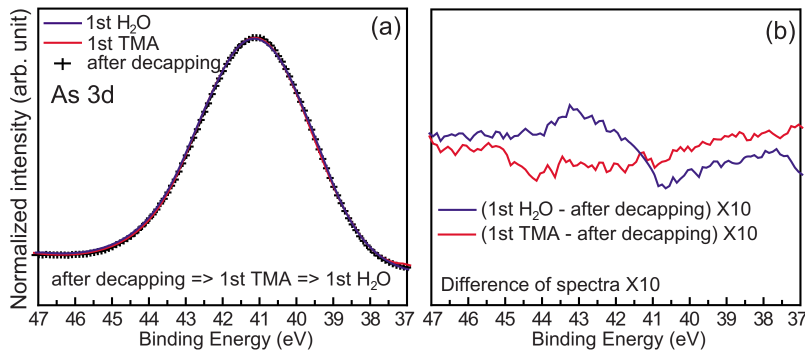

FIG. 2. (Color online) (a) Smoothed and normalized (by the maximum intensity) As 3*d* spectra for TMA-first dosing, taken after decapping of $In_{0.53}Ga_{0.47}As$, 1st TMA pulse, and the subsequent 1st H_2O pulse. (b) Difference in XPS As 3*d* spectra relative to the decapped sample for the TMA and H_2O/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.

(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_2O_3 is less than one monolayer per cycle,[6,7] 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_2O pulses and the background residual moisture present in an ALD system that uses H_2O as an oxidant.[8] The absence of detectable group III and group V oxides at the ALD-$Al_2O_3/In_{0.53}Ga_{0.47}As$ interface[4] suggests three possibilities—(i) strong resistance of the as-decapped $In_{0.53}Ga_{0.47}As$ to oxidation by $H_2O(g)$, (ii) strong resistance of the decapped $In_{0.53}Ga_{0.47}As$ to oxidation by $H_2O(g)$ after initial TMA dosing, or (iii) repeated partial oxidation of the surface followed by "clean-up" of the oxide during TMA exposure.

To test the first scenario, multiple pulses of H_2O 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_2O dosing (referred to as pre-H_2O), 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_2O 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_2O 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_2O_3.[9] However, as discussed below, there may be contributions to the higher binding energy peak from suboxides or hydroxyl species, AsO_xH_y. The subsequent TMA pulse (1st TMA) reduced the intensity of the higher binding energy tail, suggesting the reduction in AsO_x/AsO_xH_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_2O dosing are essentially identical, indicating that the H_2O dosing was not capable of forming an In oxide stable at the 270 °C ALD temperature.

In contrast to H_2O-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_2O/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 susceptibile to oxidation by H_2O pulses, while the decapped surface treated with the initial TMA pulse remained unaltered upon a pulse of H_2O, proposed model (ii) [strong resistance of the decapped to oxidation by $H_2O(g)$ 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_2O, 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_2O.

Even though TMA dosing reduces As oxide/hydroxide formed by initial H_2O exposure, the sequence of ALD precursors introduced (i.e., TMA-first versus H_2O-first) is still critical, as illustrated in Fig. 3. H_2O-first ALD-Al_2O_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_2O-first sample compared to the TMA-first sample.[10]

A major concern with the H_2O-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 $In_{0.53}Ga_{0.47}As(001)$-$(4\times2)$ 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_2O vapor at 10–100 mTorr and 25 °C for 1 to 2 min,

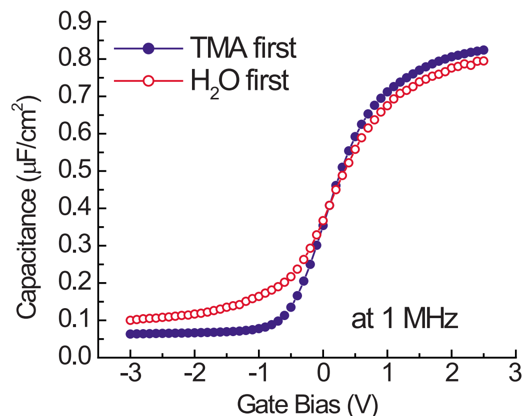

FIG. 3. (Color online) CV curves taken at 1 MHz ac frequency from MOS capacitors consisting of Pt/ALD-$Al_2O_3/In_{0.53}Ga_{0.47}As(001)$ whose ALD process was initiated by TMA (filled circle) or H_2O (empty circle).

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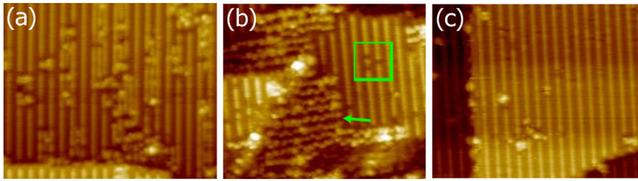

FIG. 4. (Color online) STM data of the H_2O-dosed InAs(001)-(4×2) surface as a function of temperature. (a) 200 °C. Reaction results in interstitial rows parallel to the substrate rows. (b) 350 °C. Regions of the $\alpha2(2\times4)$ reconstruction are apparent. (c) 450 °C. The clean InAs(001)-(4×2) surface is regenerated. All images are filled state, ~25×35 nm^2.

and the samples were subsequently annealed in UHV. Note that the ALD experiments were performed with 270 °C H_2O dosing, which may produce slightly different As oxides. The clean InAs(001)-(4×2) surface consists of row and trough features oriented in the [110] direction. After annealing the H_2O dosed surface at 200 °C, the H_2O induced reaction sites appear in the trough regions [Fig. 4(a)]. The H_2O-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 $\alpha2(2\times4)$ reconstruction.[12] Due to the presence of these surface As vacancy cuts in the rows and the $\alpha2(2\times4)$ reconstruction, it is likely that As atoms are displaced by the reaction of the InAs substrate with H_2O and diffuse on the surface to form areas of $\alpha(2\times4)$ 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 $In_{0.53}Ga_{0.47}As(001)$ surface, it is expected that the H_2O dosing on the decapped $In_{0.53}Ga_{0.47}As(001)$ 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 H_2O.

The XPS results show that after H_2O 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 As_2 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: $H_2O(g) + InGaAs(001)-(4\times2) \rightarrow AsO_xH_y/InGaAs(001)-(4\times2) \rightarrow As_2/InGaAs(001)-(4\times2) + H_2O(g) \rightarrow InGaAs(001)-(4\times2)$. Although a subsequent TMA pulse at modest temperature (270 °C) is also capable of reducing AsO_xH_y formed by the initial H_2O 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 distinguish from the bulk As in InGaAs. However, both the dangling bonds and the displaced As atoms created by H_2O dosing are expected to provide electrically active interface states in MOS devices,[3] consistent with the CV results shown in Fig. 3.

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