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Reversible and irreversible reactions of three oxygen precursors on $InAs(0\ 0\ 1)-(4\times 2)/c(8\times 2)$

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ABSTRACT

The substrate reactions of three common oxygen sources for gate oxide deposition on the group III rich InAs (0 0 1)- $(4 \times 2)/c(8 \times 2)$ surface are compared: water, hydrogen peroxide (HOOH), and isopropyl alcohol (IPA). Scanning tunneling microscopy reveals that surface atom displacement occurs in all cases, but via different mechanisms for each oxygen precursor. The reactions are examined as a function of post-deposition annealing temperature. Water reaction shows displacement of surface As atoms, but it does not fully oxidize the As; the reaction is reversed by high temperature (450 °C) annealing. Exposure to IPA and subsequent low-temperature annealing (100 °C) show the preferential reaction on the row features of InAs(0 0 1)- $(4 \times 2)/c(8 \times 2)$, but higher temperature anneals result in permanent surface atom displacement/etching. Etching of the substrate is observed with HOOH exposure for all annealing temperatures. While nearly all oxidation reactions on group IV semiconductors are irreversible, the group III rich surface of InAs(0 0 1) shows that oxidation displacement reactions can be reversible at low temperature, thereby providing a mechanism of self-healing during oxidation reactions.

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1. Introduction

III-V materials are being investigated for use in metal-oxidesemiconductor field effect transistors (MOSFETs) due to their high electron mobility compared to silicon and their tunable bandgaps. Consequently, growth of metal oxides on III-V semiconductor surfaces is a very active area of research [1–8]. Of the many thin film deposition techniques, atomic laver deposition (ALD) has received much attention for nanoscale films due to its precise control of film growth over large areas. However, for most III-V materials, it is critical to fully oxidize the gate metal while avoiding oxidation of the substrate since a low defect density interface with an unpinned Fermi level is required for operable MOSFET devices. For III-V surfaces, a metal precursor-first ALD technique is employed to reduce substrate oxidation, but less than one monolayer of metal is deposited due to bulky ligands on the precursors. Therefore, adventitious oxidation of the substrate by the oxygen precursor must still be avoided. In this study, three different oxygen precursors (H₂O, HOOH, and IPA) were investigated for adventitious substrate oxidation and disruption of the $(4 \times 2)/c(8 \times 2)$ surface of InAs(001). Atomic layer deposition growth of oxides usually employs water as the oxygen precursor [9,10], but other oxygen precursors have been utilized less frequently, including hydrogen peroxide (HOOH) [11-13] and propan-2-ol (isopropyl

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alcohol or IPA) [14–16]. Studies have shown that the choice of precursor greatly affects the quality of the film [17–19].

Indium arsenide is a low bandgap, high electron mobility III-V material. The (0 0 1) surface is the technologically important crystallographic orientation upon which most epitaxial growth is performed. There are many different reconstructions of this surface. These range from the As-rich series of reconstructions like the $\alpha 2$ (2×4) and the $\beta 2(2 \times 4)$ [20–22], to the In-rich reconstructions also known as the $\beta 3(4 \times 2)$ or $\beta 3'(4 \times 2)$ [23–25]. A key feature of the (2×4) reconstructions is the presence of As dimers, which have been shown to facilitate the reaction of O₂ on other III–V surfaces [26,27]. The In-rich (4×2) surface reconstruction lacks surface As dimers and has been shown to be much less reactive to molecular oxygen [28] and is therefore, likely to be more suitable for oxide growth. The ability to produce high quality, low defect density $InAs(0\ 0\ 1)-(4\times 2)/c(8\times 2)$ surfaces makes this surface an excellent substrate for scanning tunneling microscopy (STM) studies. It also closely resembles another important III–V semiconductor surface, $In_{0.53}Ga_{0.47}As(0\ 0\ 1)-(4\times 2)/c$ (8×2) [29]. Since the InAs $(0 \ 0 \ 1)$ - (4×2) surface is nearly identical to the $In_{0.53}Ga_{0.47}As(0\ 0\ 1)-(4\times 2)$ surface but has better order, it is preferable for STM studies. The reactions on these two surfaces are likely very similar. Other studies have examined the effects on III-V substrates of using H₂O as the oxygen precursor for ALD [10,19,30,31]. Those researchers explored oxidation of the groups III and V atoms of similar semiconductor surfaces, using X-ray photoelectron spectroscopy (XPS) and scanning transmission electron microscopy (STEM), and the subsequent self-cleaning effects of the oxides by exposure to

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the metal ALD precursor. The research presented in this study is complimentary to those studies, since that research employed wet chemistry passivated surfaces without attention to the specific surface reconstructions of the III–V substrates. In this study, ultra-high vacuum (UHV)-prepared MBE-grown surfaces are used with strict attention to the surface reconstructions in order to elucidate the types of mechanisms occurring during the oxidation and functionalization of the III–V surface.

2. Methods

The experiments were performed in a UHV chamber equipped with an Omicron low-temperature scanning tunneling microscope (STM), a Perkin Elmer model 11-500A Auger electron spectrometer (AES), and an Omicron SpectraLEED low energy electron diffractometer (LEED). The base pressure was 2×10^{-11} Torr. Growth on 2 in. InAs(0 0 1) substrates was carried out in a separate DCA 450 solid source MBE system. The growth rate used was 0.4 monolayers/s, determined by RHEED intensity oscillations during homoepitaxy, at a temperature just below the transition of the (2×4) to (4×2) surface. A mixture of As₂ and As₄ was used as the group V species. Si and Be were used as n- and p-type dopants, respectively. The MBE-grown layers were 300 nm thick, and the doping concentration was 1×10^{18} cm⁻³. To protect the surface during shipment, arsenic capping (60-80 nm thick) was carried out by having the substrate cooled to below room temperature in As₂ flux at 25 °C, and deposition was continued for 1-2 h at which time RHEED showed a diffuse background. The capped wafers were shipped in a rough vacuum container for STM studies. After transfer into the UHV analysis chamber, the InAs samples were degassed at 200 °C for 3 h and subsequently, heated to 380 °C for 2 h to desorb the As₂ capping layer. Capping layer desorption was evidenced by a pressure rise to ~1×10⁻⁸ Torr. The InAs(0 0 1)-(4×2)/ $c(8\times2)$ reconstruction was formed by increasing the substrate temperature by 0.2 °C s⁻¹ to 450 °C and holding for 10 min. The formation of the $(4 \times 2)/c(8 \times 2)$ surface at 450 °C is consistent with other studies that used different temperature monitoring techniques [23,32,33]. In this study, the temperature was monitored using a thermocouple in contact with the sample heater stage. To obtain the (2×4) reconstruction of the InAs(0 0 1) surface, a different degassing-decapping-annealing process was employed. The degas cycle was performed at 180 °C for 3 h followed by 300 °C for 2 h and finally a 360 °C anneal for 45 min. The extended annealing step at 300 °C was necessary for desorption of the protective As₂ capping layer at lower temperatures. The 360 °C annealing temperature is in general agreement with other studies using UHV annealing to obtain the InAs(001)- (2×4) surface [21,34]. Surface periodicities for all reconstructions were confirmed using LEED and STM. Although deviations from the noted annealing temperatures are likely to exist due to the temperature monitoring technique, STM and LEED results routinely showed that these methods produced the desired surface reconstructions.

The InAs substrates were transferred from the UHV chamber into a high vacuum chamber ($P \cong 5 \times 10^{-7}$ Torr) for dosing with oxygen precursors. The oxygen precursors were HPLC grade H₂O, HPLC grade IPA and 30% HOOH in H₂O (HOOH_(aq)). The pure vapor was prepared in a clean dosing line at room temperature over ~5 ml of the liquid in a reservoir at 25 °C. The desired vapor dose was prepared by throttling the pumping speed on the dosing line and reservoir through a leak valve and subsequently, flowing this vapor into the dosing chamber through a shut off valve. The dosing pressure was 10–100 mTorr for a time of about 1 min. After dosing, the samples were re-introduced into the UHV chamber and annealed. The range of annealing temperatures was chosen to mimic typical oxide deposition and post-deposition annealing conditions – from 100 °C to 450 °C. After dosing the surface with any of the oxygen precursors, the samples required an annealing temperature of at least 100 °C in UHV before

analysis by STM. Presumably, this is due to the large amount of physisorbed material that remains on the surface and interacts with the STM tip after dosing under these conditions. For practical gate oxide ALD, oxidant dosing is almost always performed on InAs or InGaAs at 250 °C to 280 °C while the studies in this report involve dosing oxidants at 25 °C followed by high temperature annealing. This allows the separation of the defect generation and defect repair processes to be isolated since reactions at elevated temperature occur too rapidly to be readily imaged by STM. Furthermore, the defect generation process because it occurs in post-deposition annealing (PDA) [3,35,36].

Filled (empty) state STM images were acquired at -1.50 V to -2.50 V (+2.50 V) sample bias relative to the electrochemically etched W tip. The constant-current images were taken at a tunneling current setpoint of 50–200 pA. Determination of the adsorbate coverage in the STM images was done via the ratio of pixels in the 512×512 images associated with the adsorbed surface area versus the full image size.

3. Results and discussion

The InAs(0 0 1)-(4×2)/ $c(8\times2)$ surface has been imaged using STM by this research group, and the results are discussed elsewhere [25]. The clean surface is modeled as consisting of rows of In atoms along the [1 1 0] direction divided by trough regions that contain two In–In dimers per unit cell in the 3rd atomic layer; there are no As dimers on this surface. This surface reconstruction is known as the $\beta 3'(4\times2)$ reconstruction of the InAs(0 0 1)-(4×2)/ $c(8\times2)$ surface. Feldwinn et al. [25] discuss the possibility that the $\beta 3'(4\times2)$ reconstruction may be a superposition of two similar reconstructions that differ only in minor details within the row structure, similar to what is discussed in Shen et al. [29] for In_{0.53}Ga_{0.47}As(0 0 1)-(4×2).

For any oxide deposition technique on InAs or InGaAs, the role of the oxidant precursor is to either make the substrate reactive to the metal precursor or to convert any metal precursor to metal oxide since it is always unfavorable to covert the substrate to oxide via irreversible displacement reactions. With oxidant-first ALD, the only purpose of the oxygen precursors is to initiate the ALD reaction by functionalizing the semiconductor surface with hydroxyl ligands without oxidizing or disrupting the surface. The hydroxyl ligands are in turn reactive to the ALD metal precursors such as trimethyl aluminum. On the subsequent pulse, the metal ALD precursor attacks the O atom of the –OH group, substituting for the H atom [37,38]. A good oxygen precursor reaction is one which only results in formation of the substrate–OH bonds; this is mostly likely when the precursor has a reactive R–OH bond, where the R group is a good leaving group upon formation of the substrate–OH bonds.

The InAs(001)- $(4 \times 2)/c(8 \times 2)$ surface exhibits different reactivity towards the three oxygen precursors examined in this study. Fig. 1 illustrates this with a comparison of the annealed InAs surface after reaction with equivalent doses from all three oxygen precursors. The vapor pressure and exposure times for the three precursors were similar, and dosing was followed by one minute anneals at 200 °C in UHV. The result of the H₂O dose is shown in Fig. 1a and represents a coverage of ~0.05 ML. This is very similar to the coverage obtained by the IPA dose, which is ~0.07 ML and shown in Fig. 1b. However, the HOOH dose resulted in a much higher coverage of 0.44 ML, which is shown in Fig. 1c. Therefore, the 30% HOOH(aq) solution produces a vapor that reacts with the semiconductor surface much more readily than either pure H₂O or IPA. This is likely due to the difference in R–OH bond energy of the three precursors. For hydrogen peroxide this energy is only 2.18 eV, whereas for IPA and water, the R-OH bond dissociation energies are 4.12 eV and 5.15 eV, respectively [39].



Fig. 1. Reactivity comparison between the three ALD oxygen precursors. The coverage shows the different reactivities on the InAs(0 0 1)- $(4\times2)/c(8\times2)$ surface. a) The post-annealed, H₂O-exposed surface showing the coverage is about 0.05 ML (STM image + 2.50 V, 50 pA, 780 Å × 780 Å). b) The post-annealed, IPA-exposed surface showing the coverage is similar to that of the H₂O dosed surface; it is about 0.07 ML (STM image -2.50 V, 200 pA, 870 Å × 870 Å). c) The post-annealed, HOOH-exposed surface showing the coverage is about 0.44 ML. (STM image -2.5 V, 50 pA, 780 Å × 780 Å). All exposures (\gg 10⁴ L) and subsequent annealing temperatures and times (200 °C for ~1 min) were equal.

3.1. The water-dosed surface

The clean InAs surface prior to H_2O exposure is shown in Fig. 2a. At sub-ML coverages, the $H_2O/InAs(0\ 0\ 1)-(4\times 2)/c(8\times 2)$ surface exhibits ordered features in the [1 1 0] direction centered between

the In rows called "interstitial rows," as shown in Fig. 2b. Although not atomically resolved, the adsorbates are centered between and at the same apparent height as the adjacent In rows; a bonding structure for this overlayer was not determined, but the height of the adsorbate interstitial rows is consistent with the bonding of OH or displaced As



Fig. 2. STM data for the $H_2O/InAs(001)-(4\times2)/c(8\times2)$ reaction at different annealing temperatures. a) The clean InAs surface before H_2O exposure. The blue boxes highlight the T defects [23,28]. STM data 870 Å × 870 Å, filled state. b) The same surface after H_2O exposure and subsequent 200 °C anneal. The inset (180 Å × 50 Å) shows the prevalent feature for these conditions, called the interstitial rows. STM data 870 Å × 870 Å, filled state. c) The same H_2O -exposed surface after annealing to 350 °C. The main features for these conditions are zig-zag rows in the [-110] direction (shown in the inset, 70 Å × 120 Å) and cuts in the rows (highlighted by the green boxes). STM data 870 Å × 870 Å, filled state. d) The same surface after annealing to 450 °C. All regrowth and row cut features are gone from the surface. The T defects are highlighted by the blue boxes and are present at densities similar to the clean surface (left lower inset, 60 Å × 60 Å). STM data 870 Å × 870 Å, filled state.

atoms to trough In atoms. At this coverage, the length of these interstitial rows can be longer than 280 Å, consistent with attractive long range order.

Analysis of Fig. 2b reveals that the regrowth resulting from the H₂O dose constitutes an area of 2600 nm² of the full 7570 nm², or 34% of the image area, which is shown in Fig. 3a. A histogram of the STM data from Fig. 2b reveals a bimodal distribution of heights of the STM pixel data (see Fig. 3b). The first mode of the distribution corresponds to only the unreacted trough structures on InAs(0 0 1)-(4×2)/c(8×2). The remaining part of the distribution represents both the rows on the InAs(0 0 1)-(4×2)/c(8×2) surface and the H₂O-induced regrowth, including the interstitial rows. It was determined that regrowth *above* both the interstitial and In rows accounts for the highest 9% of the interstitial rows combined with the other 1st layer regrowth account for 25% of the image area. This is summarized in Fig. 3b.

Upon annealing the H₂O-dosed surface to 350 °C, a new ordered structure is observed, as shown in Figs. 2c and 4a. The structure forms zig-zagging rows in the $[-1\ 1\ 0]$ direction that are separated by about 16–18 Å in the [1 1 0] direction and consist of lobes that are separated by about 8-9 Å in the $[-1\ 1\ 0]$ direction (along the length of the new rows). This new ordered structure is consistent with regrowth of the $\alpha 2(2 \times 4)$ reconstruction of the clean InAs(001) surface, which is stable at lower temperatures than the $\beta 3'(4 \times 2)$ reconstruction and lower As flux than the $\beta 2(2 \times 4)$ reconstruction [21,40]. For comparison, an as-prepared (2×4) surface is shown in the STM data in Fig. 4b. Ball-and-stick diagrams for the $\beta 3'(4 \times 2)$ and the $\alpha 2(2 \times 4)$ reconstructions of the InAs(0 0 1) surface are shown in Fig. 4c and d. The as-prepared (2×4) surface consists of mostly $\alpha 2(2 \times 4)$ reconstruction with some $\beta 2(2 \times 4)$ reconstruction present [22,40]. The zig-zagging rows of the $\alpha 2(2 \times 4)$ reconstruction of InAs(0 0 1) are also separated by about 16–18 Å in the [1 1 0] direction and consist of lobes that are also separated by about 8-9 Å along the length of the rows. It appears that the H₂O-induced $\alpha 2(2 \times 4)$ regrowth on the $\beta 3'(4 \times 2)$ surface initiates at step edges. Further evidence suggesting that this is $\alpha 2(2 \times 4)$ regrowth is that within the surface unit cells for both the $\beta 3'(4 \times 2)$ and the $\alpha 2$ (2×4) reconstructions, there are the same number of As and In atoms. No change to the surface As:In ratio is required for the transition between the two reconstructions.

After H₂O exposure followed by 350 °C annealing, row cut features are observed. These row cut features are highlighted in the STM data by the green boxes in Fig. 2c. One possible explanation is that the cuts are the result of substrate surface As displacement or In displacement. Additionally, O₂ chemisorption has been shown to cause dark cut features (also via surface As displacement) upon exposure to molecular oxygen at 25 $^{\circ}$ C [28]. The vapor pressure of pure As₂O₃ at 350 °C is 141 Torr [41], so for the 350 °C annealed surface, if any As₂O₃ formed due to H₂O exposure on the InAs surface, it would likely have evaporated. Furthermore, the 350 °C annealed, H₂O-dosed surface showed no evidence for the presence of oxygen within the detectable limits of AES for coverages of ~0.1 ML. Therefore, the cuts in Fig. 2c are likely due to As displacement, and by 350 °C nearly all oxygen is removed from the surface. The H₂O exposed and 350 °C annealed InAs $(0 \ 0 \ 1)$ - $(4 \times 2)/c(8 \times 2)$ surface shows regions of the $\alpha 2(2 \times 4)$ reconstruction. Therefore, rather than oxidizing the surface As, the initial reaction of H₂O on InAs(001)- $(4 \times 2)/c(8 \times 2)$ displaces surface As atoms. The water/oxygen desorption at 350 °C could occur via two distinct mechanisms: H₂O could directly evaporate from the surface, or the -OH chemisorbed species could recombine and undergo evaporation as $2(OH) \rightarrow H_2O + \frac{1}{2}O_2$.

After annealing the surface to 450 °C, the clean InAs(0 0 1)-(4×2)/ $c(8\times2)$ surface is regenerated; there are neither row cut features nor $\alpha 2(2\times4)$ regrowth present (Fig. 2d). This high annealing temperature is the same temperature that is used to prepare the clean surface in UHV from the MBE-grown and As₂-capped samples. If the As dimers were to evaporate, excess In would remain on the surface and there would be evidence of this in the STM data for the (4×2) surface in the form of amorphous metallic islands. A comparison of the STM data for the InAs(0 0 1)-(4×2)/ $c(8\times2)$ surface before and after the H₂O exposure and 450 °C anneal shows the same amount of amorphous island features; Fig. 2a and d each have 2% island coverage. The lack of row cut features is also evident when comparing Fig. 2a and d. The T defect is distinct from a row cut feature. The T defect [23,28] causes a local depression in both adjacent rows and is shown in the inset of Fig. 2d and indicated by blue boxes in Fig. 2. A row cut is more



Fig. 3. Height analysis from $H_2O/InAs(0\ 0\ 1)-(4\times 2)/c(8\times 2)$ reaction with a 200 °C anneal from the STM data in Fig. 2b. a) Only the regrowth areas are shown, with the clean InAs surface data subtracted from the STM image (870 Å×870 Å, filled state). This constitutes 34% of the image area. b) A histogram of the heights in the STM pixel data from Fig. 2b, which shows a bimodal distribution. The 1st layer regrowth accounts for 25% of the image area and the remaining 9% of the regrowth consists of 2nd layer regrowth and above.



Fig. 4. H₂O-induced regrowth on InAs(0 0 1)-(4×2)/ $c(8\times2)$ vs. the as-prepared (2×4) reconstruction. a) STM image (130 Å×170 Å, -1.80 V, 100 pA) of the H₂O-induced regrowth after 350 °C anneal on InAs(0 0 1)-(4×2)/ $c(8\times2)$. b) STM image (120 Å×160 Å, -2.0 V, 100 pA) of the InAs(0 0 1)-(2×4) surface. The black box surrounds an $\alpha 2(2\times4)$ region and the red box surrounds a $\beta 2(2\times4)$ region [22]. c) and d) Top-down ball-and-stick diagrams of the $\beta 3'(4\times2)$ and $\alpha 2(2\times4)$ reconstructions of the InAs(0 0 1) surface, respectively. Only the uppermost atomic layers are shown for clarity. Note that each surface reconstruction contains 4 surface As atoms and 6 surface In atoms per unit cell.

pronounced with sharper boundaries and does not have a corresponding depression in adjacent rows, and is centered on the row rather than in the trough. Therefore, during the 450 °C anneal, the displaced As dimers rearrange on the InAs(0 0 1) surface to form the thermodynamically stable $\beta 3'(4 \times 2)$ reconstruction.

The PDA step involved in ALD with H_2O as the oxygen precursor for high- κ oxides shows an improvement in the C–V characteristics of MOS structures grown on the same or similar III–V surfaces [3,35,36]. This is consistent with the process described above, where any displacement of surface As by the H_2O during ALD is healed upon annealing, lowering the defect density at the III–V surface that may lead to Fermi level pinning.

3.2. The isopropyl alcohol-dosed surface

For low coverage (<0.25 ML), after exposure of the clean InAs(0 0 1)-(4×2)/ $c(8 \times 2)$ surface to IPA, followed by annealing to 100 °C, the STM results show that reaction occurs selectively on the In rows along the [1 1 0] direction. The combination of IPA exposure and 100 °C anneal was the only oxygen precursor examined that showed site-selective bonding to the InAs surface. Attempts were made to acquire STM data after using only 100 °C as the annealing temperature for the studies using H₂O and HOOH, but these were not successful. Presumably, this is due to physisorbed material on the surface that interacts undesirably with the STM tip and which is *not* present after using IPA with a 100 °C anneal.

Fig. 5 shows three STM images of the InAs(0 0 1)- $(4\times 2)/c(8\times 2)$ surface after successive IPA doses and 100 °C anneals for ~1 min. Fig. 5a shows the site-selectivity of IPA for the row features at low coverage. It is assumed that the adsorption occurs via dissociation of the R–OH bond and chemisorption of the –OH (hydroxyl) group onto the InAs surface. The coverage shown in Fig. 5b was obtained after 3 consecutive doses of $\gg 10^6$ L each and 100 °C anneals. Only after the 4th dose/anneal cycle was full coverage (~1 monolayer) obtained (as shown in Fig. 5c); this corresponds to an irreversible chemisorption probability of less than 10^{-6} . Since the bond dissociation energy of the R–OH group in IPA is 4.12 eV, most of the incident IPA molecules may not dissociate upon physisorption and may only evaporate during the annealing cycle, rather than undergoing dissociative chemisorption. Additionally, there is a large amount of steric hindrance around the hydroxyl group of the IPA molecule. This may contribute to the low reactivity by restricting access to the frontier orbitals of the O atom by the substrate electrons, except with preferred orientations. Additionally, a physisorbed IPA molecule will sterically hinder other incident IPA molecules from approaching the substrate and dissociatively chemisorbing.

After formation of the first ML, the surface remains very flat with an RMS roughness of 0.7 Å. The RMS roughness of the clean surface is also about 0.7 Å. The similarity in RMS roughness of clean InAs(0 0 1)- $(4 \times 2)/c(8 \times 2)$ is due to the highly corrugated row and trough structure, whereas the terminated surface tends to fill in the trough structure, even though some second layer growth may occur. Auger electron spectroscopy of the full coverage surface reveals the relative concentrations of the surface species (for Auger depth); the AES spectrum is shown in Fig. 5d. The AES results confirm the presence of O and C on the surface at a ratio of 1:2. The presence of C on the surface is likely due to carbon contamination from the IPA, although if all –OH and $(CH_3)_2$ CH ligands remained on the surface stoichiometrically, the O:C ratio should be 1:3 instead of 1:2. However, the AES process itself may also deposit C onto the surface. Remaining carbon from the IPA could be detrimental to the high- κ oxide film in ALD process [42].

The selective bonding by IPA at 100 °C may suggest a lack of substrate atom displacement, with low surface roughness, and an – OH terminated substrate for the ALD initiation reaction. Water and trimethyl aluminum (TMA) precursors have been used for alumina growth on Si(1 0 0) with an optimum temperature of 177 °C [43] and even lower temperatures (<100 °C) have been used with some success for ALD of alumina [14,44]. However, typical ALD conditions use higher temperatures such as 200 °C to 400 °C for Al₂O₃ using TMA and IPA [15,16] and similar temperatures using H₂O instead of IPA as the O precursor [9,30] so the stability of OH termination at higher temperatures is critical.



Fig. 5. 25 °C reaction followed by 100 °C anneal of IPA with $InAs(0 \ 0 \ 1) - (4 \times 2)/c(8 \times 2)$ surface as a function of IPA exposure. a) STM image (390 Å × 390 Å, $-2.50 \ V$, 100 pA) at low coverage, showing preference for reaction on the rows. The RMS roughness is 0.71 Å. b) STM image (390 Å × 390 Å, $-2.50 \ V$, 50 pA) at medium coverage regime with an RMS roughness of 0.73 Å. Reaction occurs in the trough region of the surface as well as on the row. c) STM image (390 Å × 390 Å, $-2.50 \ V$, 50 pA) at high coverage; no clean InAs surface is visible. The RMS roughness is 0.65 Å. d) The AES spectrum from the surface in Fig. 5c, indicating the presence of both C and O at the energies of 272 eV and 503 eV (arrows), respectively. The relative concentrations of the surface elements are In = 0.46, As = 0.39, O = 0.05, and C = 0.10 for the region of the surface sampled by the Auger technique.

Annealing between 200 °C and 450 °C for IPA coverage on InAs(0 0 1)- $(4 \times 2)/c(8 \times 2)$ resulted surface reactions that are inconsistent with simple OH termination at these temperatures (Fig. 6). Although the nucleation density for the 200 °C annealing temperature is still high (Fig. 6a), there is evidence for second layer growth. The line trace profile for Fig. 6a is shown in Fig. 6d (blue lines). Regrowth is seen to exist up to 5 Å above the row height of the InAs surface. Additionally, substrate atom displacement is evident in the STM data for Fig. 6a–c showing dark pits in the surface. Pits are evidenced in the red line scan profile in Fig. 6d, which is for Fig. 6b, since the surface height drops *below* the trough height for the clean InAs surface. This was not evident in the IPA-dosed, 100 °C annealed surface.

A change in the nucleation density is apparent after annealing the surface to 350 °C. As shown in Fig. 6b, the island size increases dramatically and multilayer growth occurs. Row cut atom displacements (indicated by the green boxes) are observed, which are likely the same defects as the row cuts seen after H_2O dosing followed by 350 °C anneals, shown in Fig. 2c. However, in the case of IPA dosing, these row cuts are *not* healed upon annealing to 450 °C as they are in the case of H_2O dosing.

To determine if irreversible displacement of surface atoms occurs after IPA dosing, the surface was annealed to 450 °C as shown in Fig. 6c. The row cut features are still present (green boxes) as are the pits (blue arrows). The nucleation density of regrowth is lower for the surface in Fig. 6c than for the lower annealing temperatures, and the regrowth is concentrated at domain boundaries and pits. Since the regrowth is concentrated at certain regions of the surface, it is difficult to determine if the total amount of regrowth has declined after high temperature annealing. This is due to the small areal selectivity of STM and the relatively large size and specific density of the grain boundaries. Comparison of the 450 °C annealed surfaces for IPA dosing (Fig. 6c) and H₂O dosing (Fig. 2d) shows that annealing of IPAdosed InAs(0 0 1)-(4×2)/ $c(8\times2)$ does not restore the clean surface morphology, in contrast to annealing of H₂O dosed InAs(0 0 1)-(4×2)/ $c(8\times2)$. Therefore, As displacement is irreversible for IPA dosing of InAs(0 0 1)-(4×2)/ $c(8\times2)$. In contrast to the H₂O-dosed surface, the IPA-dosed surface showed the presence of carbon. The role of C in the displacement of surface atoms is not known for this case. It is possible that the mechanisms of surface atom displacement are not independent of the presence of carbon for the case of IPA dosing. However, the row cut features are very similar to the row cut features seen in both the H₂O and HOOH dosing experiments.

3.3. The hydrogen peroxide-dosed surface

Of the three oxygen precursors examined in this study, HOOH was the most reactive on the InAs surface. This is expected since the peroxide bond is much more reactive than either the H–OH bond of water or the secondary alcohol $(CH_3)_2$ HC–OH bond of IPA; the HO–OH bond dissociation energy is only 2.18 eV [39]. In Fig. 1c, the HOOH-dosed InAs surface shows the most surface reaction from an equivalent dose of the other O precursors. At low coverage and 200 °C anneal, single reaction sites are observed in STM, as shown in Fig. 7a. These reaction sites occur in the trough region of InAs(0 0 1)-(4×2)/c(8×2). Line scans of the data show that the adsorbates bond in the trough region ~9 Å apart in the [1 1 0] direction and ~6 Å from the In row. This is consistent with forming hydroxyl bonds to the In atoms involved in the trough dimers.



Fig. 6. STM data for IPA dosing at 25 °C and subsequent annealing. a) The 200 °C annealed surface shows high nucleation density and the onset of 2nd layer growth. b) The same surface after annealing to 350 °C shows lower nucleation density, but the clear presence of multilayer growth (green arrows), row cut features (green box), and pits in the surface. c) The same surface after annealing to 450 °C shows that some of the multilayer regrowth (green arrows) is gone from the surface, but the pits (blue arrows) and row cut features still remain. d) The line scan profile data for the blue and red line scans from a) and b). All STM data are 870 Å × 870 Å, filled state.

Additionally, there is 2nd layer (and higher) growth reaction sites grouped in clusters. This is in contrast to the H₂O-dosed surface where the reaction is much more ordered and tends to be mostly 1st, with some 2nd layer growth, where the 1st layer growth is ordered and centered in the trough region. Although the vapor from 30% HOOH_(aq) contains H₂O, most of the reaction appears to be due to HOOH rather than H₂O. At higher doses of HOOH, there is very little site-selectivity that was seen for the case of water alone (Fig. 7b). The data show that InAs(0 0 1)-(4×2)/c(8×2) undergoes oxidation (at a variety of sites) more readily when dosed with 30% HOOH_(aq) as opposed to H₂O or IPA.

Extreme disorder is observed upon annealing at 350 °C. The surface becomes pitted and amorphous islands (mounds) appear in STM images as shown in Fig. 7c. The topology ranges from about 6 Å below the clean InAs surface to about 4 Å above the surface, as shown in the line scan in Fig. 7e. Since arsenic oxides are quite volatile at this temperature [41] and HOOH is a very good oxidizer, it is likely that the surface As atoms become oxidized and evaporate upon annealing at 350 °C, leaving the surface disordered. The surface indium is also likely oxidized. The extent of this is clearly evident in Fig. 7c, in which there are large pits, 100–500 Å in size, adjacent to the amorphous mounds that are similar in size. AES reveals the presence of O on the surface. As₂O₃ is quite volatile [41], but indium oxides are not [45]; therefore, the surface As is removed, but the In remains, in the form of In₂O₃ or In sub-oxides. This process forms the pits and mounds seen in STM. Additionally, no regions of the $\alpha 2(2 \times 4)$ reconstruction are

observed in STM data after HOOH and 350 $^{\circ}$ C anneal, as in the case of the H₂O-dosed, 350 $^{\circ}$ C annealed surface (Section 3.1). This indicates that the surface As is *not* simply being displaced.

After annealing to 450 °C, the extreme disorder observed after annealing to 350 °C is partially removed. The clean InAs(0 0 1)- $(4 \times 2)/c(8 \times 2)$ reconstruction is mostly restored with the exception of the row cut features (green boxes in Fig. 7d); however, the surface has been etched, leaving behind "gaps" in the surface layer. This is shown in the lower section of Fig. 7d where two large, single-layer "gaps" are seen that are about 400 Å wide and separated by only two surface unit cells in the [-1 1 0] direction. These features are *not* seen on the MBE-grown surfaces and are consistent with surface etching. Other STM data for this surface show more large single-layer pits that are not seen on the clean surface and also consistent with etching.

The disappearance of the oxide mounds that are formed by 350 °C annealing (Fig. 7c) is consistent with them having an indium oxide composition. Bulk In_2O_3 evaporates incongruently as In_2O and O_2 [46,47] and In_2O has been shown to evaporate from surfaces in UHV around 400 °C [48]. Therefore, the mounds most likely consist of In_2O_x . The arsenic oxides created by the reaction of HOOH evaporate at temperatures less than 350 °C and the indium oxides remain in the form of amorphous mounds. When the surface is annealed to 450 °C, the mounds of indium sub-oxides evaporate. Not all of the oxidized In is a suboxide. Some regrowth islands still remain after the 450 °C anneal, as indicated by the blue boxes in Fig. 7d. These islands could be In_2O_3 , and it would indicate that the oxidation by HOOH produces



Fig. 7. STM data for HOOH dosing at 25 °C and subsequent annealing. a) At low coverage and 200 °C anneal, the reaction occurs on the trough In dimers, in addition to a variety of other sites (STM data 60 Å×60 Å, filled state). b) At coverages of almost 1 ML, the surface reaction occurs in a multilayer fashion at a variety of surface sites for annealing temperatures of 200 °C (STM data 870 Å×870 Å, filled state). c) At similar doses and a higher annealing temperature of 350 °C, the surface is etched and both multilayer pits and mounds appear on the surface (STM data 870 Å×870 Å, filled state). d) Annealing the surface to 450 °C removes much of the HOOH reaction products from the surface. Still present are the row cut features (green boxes) and a small amount of multilayer regrowth (blue boxes). The two large single-layer gaps in the lower part of the STM image are the result of etching by HOOH (STM data 870 Å×870 Å, filled state). e) The data for the line trace in c), showing that the 350 °C anneal produces regrowth mounds and also etch pits.

fully oxidized In at a rate of about 1–2 orders of magnitude lower than the suboxide.

Besides what is likely In_2O_3 regrowth (blue boxes in Fig. 7d), row cut features are also evident after the HOOH-dosed surface is annealed to 450 °C (green boxes in Fig. 7d). By comparing the dosed surfaces of all three oxidants, the origin of the row cut features can be deduced. The row cuts are present when the $InAs(0\ 0\ 1)-(4\times 2)/c(8\times 2)$ surface is annealed to 450 °C after dosing with either HOOH or IPA, or after the surface is annealed to 350 °C after dosing with HOOH, IPA, or H₂O. However, the row cuts subsequently *disappear* only from the H₂O-dosed surface after annealing at 450 °C. The 350 °C annealed, H₂O-dosed surface also shows the presence of As dimers, evidenced by the $\alpha 2(2\times 4)$ regrowth. There was no $\alpha 2(2\times 4)$ regrowth present on the IPA and HOOH-exposed and 350 °C annealed InAs surfaces. As in all ALD dosing systems, some O₂ can be present. The row cut features may be due to the

chemisorption of O₂, since similar features are seen for oxidation of the InAs(0 0 1)- $(4 \times 2)/c(8 \times 2)$ at 25 °C [28]. To test this hypothesis, the clean InAs(0 0 1)- $(4 \times 2)/c(8 \times 2)$ surface was exposed to O₂ in UHV and then annealed to 450 °C. The data are summarized in Fig. 8. Fig. 8a shows the clean surface before O2 exposure, with a domain boundary present in addition to the T defects (indicated with blue boxes). Fig. 8b is the same surface after exposure to 200 L O_2 and subsequently, annealed to 450 $^\circ C$ for 2 min. The same surface was exposed to an additional 425 L O₂ and annealed again to 450 °C for ~5 min; the results are shown in Fig. 8c. In all cases, the number of T defects (blue boxes in Fig. 8a–c) remains roughly the same (no trend of increasing T defect density) and no cut features are observed to form. Since these exposures are known to develop cut features at 25 °C, it is likely that the 450 °C annealing heals any row cuts due to O₂ that are present at lower temperatures. Therefore, the row cut features which persist to 450 °C



Fig. 8. STM data for InAs(0 0 1)-(4×2)/c(8×2) as a function of O₂ exposure and 450 °C anneals. No increase in the density of either row cut features or T defects (blue boxes) was seen. All STM images are 870 Å \times 870 Å, taken at -3.00 V and 50–100 pA. a) Clean surface. b) 200 L O₂. c) 625 L O₂.

after exposure to both HOOH and IPA are not the result of molecular oxygen that may be present during the dosing of oxygen precursors. The row cuts are likely the result of displaced As. The displacement of As is irreversible for HOOH and IPA dosing due to the formation of arsenic oxides which readily desorb on annealing, but As displacement is reversible for H₂O dosing.

4. Conclusion

The reactions of three common oxygen precursors on InAs(001)- $(4 \times 2)/c(8 \times 2)$ were investigated. The chemisorption dynamics involved indicate that different reactions occur with the III-V substrate for each precursor studied. Instead of forming a high density OH terminated surface, for all precursors examined in this study, there was evidence of substrate atom displacement that varied depending on annealing temperature. However, for the case of water, it is clearly shown that surface As is reversibly displaced, but not oxidized. The clean surface is regenerated at 450 °C. This is an important result because it shows that water does not fully oxidize the surface atoms and has the least amount of (if any) undesirable semiconductor etching for the O precursors studied.

For the case of IPA, substrate atoms are displaced, resulting in row cut features that do not heal upon annealing to 450 °C. The IPA may oxidize the displaced As, which would then evaporate from the surface during annealing. The IPA dosing does not recreate the clean InAs(001)- $(4 \times 2)/c(8 \times 2)$ surface structure after annealing at 450 °C as in the case of H₂O dosing. Pitting is also observed with IPA doses and higher annealing temperatures, which is clear evidence of substrate atom displacement/etching. However, IPA showed siteselective, first layer growth for 100 °C anneals. Furthermore, several cycles of IPA exposure plus 100 °C anneals results in a very flat reaction layer with low RMS roughness.

In the case of hydrogen peroxide, the InAs surface was etched. The As-displacement row cut features are seen, and pitting occurs at 350 °C. Both As and In are displaced and oxidized. The As oxides evaporate at low annealing temperatures, and the In₂O evaporates from the surface at temperatures above 350 °C. This process leaves large gaps in the semiconductor surface and row cut features.

The results show that none of the precursors studied would be ideal as an ALD oxidant-first initiation step on $InAs(0\ 0\ 1)-(4\times 2)$ or probably $In_{0.53}Ga_{0.47}As(001)-(4\times 2)$ since none leave an undisturbed surface with a monolayer of OH termination. For practical gate oxide ALD, oxidant dosing is almost always performed on InAs or InGaAs at 250 °C to 280 °C, while the studies in this report involve dosing oxidants at 25 °C. Dosing was followed by high temperature annealing to allow separation of the defect generation and defect repair processes for STM imaging. However, the results also show that H₂O is preferable as an ALD oxidation precursor for a metal precursor-first ALD because H₂O only displaces surface atoms rather than etching the semiconductor surface, unlike IPA and HOOH. If a PDA step is used for the deposition of gate oxides for III-V MOSFETs, the surface atom displacement will likely heal, which is consistent with literature showing that the PDA results in better C-V characteristics.

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