



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

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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)-(4×2)/c(8×2) 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)-(4×2)/c(8×2), 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-oxide-semiconductor 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 layer 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 (4×2)/c(8×2) surface of InAs(0 0 1). 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

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 α2(2×4) and the β2(2×4) [20–22], to the In-rich reconstructions also known as the β3(4×2) or β3'(4×2) [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)-(4×2)/c(8×2) 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)-(4×2)/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)-(4×2) 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 As_2 and As_4 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 $1 \times 10^{18} \text{ cm}^{-3}$. 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 As_2 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 As_2 capping layer. Capping layer desorption was evidenced by a pressure rise to $\sim 1 \times 10^{-8}$ Torr. The InAs(0 0 1)- $(4 \times 2)/c(8 \times 2)$ 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 As_2 capping layer at lower temperatures. The 360 °C annealing temperature is in general agreement with other studies using UHV annealing to obtain the InAs(0 0 1)- (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 ($P \approx 5 \times 10^{-7}$ Torr) for dosing with oxygen precursors. The oxygen precursors were HPLC grade H_2O , HPLC grade IPA and 30% $HOOH$ in H_2O ($HOOH_{(aq)}$). 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 repair process in gate oxide growth is usually separate from 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)- $(4 \times 2)/c(8 \times 2)$ 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 $\beta 3'$ (4×2) reconstruction of the InAs(0 0 1)- $(4 \times 2)/c(8 \times 2)$ surface. Feldwinn et al. [25] discuss the possibility that the $\beta 3'$ (4×2) 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 $In_{0.53}Ga_{0.47}As(0\ 0\ 1)-(4 \times 2)$.

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 convert 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(0 0 1)- $(4 \times 2)/c(8 \times 2)$ 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 H_2O 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 H_2O 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].

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