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Dual passivation of GaAs (110) surfaces using O₂/H₂O and trimethylaluminum

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The nucleation and passivation of oxide deposition was studied on defect-free GaAs (110) surfaces to understand passivation of surfaces containing only III-V heterobonds. The passivation process on GaAs (110) was studied at the atomic level using scanning tunneling microscopy while the electronic structure was determined by scanning tunneling spectroscopy (STS). The bonding of the oxidant and reductant were modeled with density functional theory. To avoid Fermi level pinning during gate oxide atomic layer deposition, a dual passivation procedure was required using both a reductant, trimethylaluminum (TMA), and an oxidant, O_2 or H_2O . Dosing GaAs (110) with TMA resulted in the formation of an ordered complete monolayer of dimethylaluminum which passivates the group V dangling bonds but also forms metal-metal bonds with conduction band edge states. These edge states were suppressed by dosing the surface with oxidants O_2 or H_2O which selectively react with group III-aluminum bonds. The presence of an ordered Al monolayer with a high nucleation density was indirectly confirmed by XPS and STS. © 2013 AIP Publishing LLC. [http://dx.doi.org/10.1063/1.4852155]

I. INTRODUCTION

Silicon based metal oxide semiconductor field effect transistors (MOSFETs) may soon reach their physical performance limits.¹ As a consequence, many alternative semiconductors are being explored for use as channel materials. III-V semiconductors are attractive channel materials due to their high electron mobilities. A limiting factor in III-V based MOSFET performance is the high-k gate oxide/III-V interface because it usually has a large density of interfacial trap states (D_{it}).² Several theories have been proposed to explain the origin of interfacial trap states.³ Studies have suggested these states are caused by native defects such as dangling bonds on the semiconductor surface, strained bonds on semiconductor surface atoms, and metal-metal bonds at the interface.⁴ The majority of III-V based MOSFETs are fabricated using the group V rich (001)-(2 \times 4) surface because this is the most easily obtained surface reconstruction.⁵ This surface usually contains at least 42% defect unit cells which prevent efficient Fermi level modulation.⁶ It may be possible to increase III-V based MOSFET drive current at low source-drain voltages by passivating the metallic In-Ga bonds and the strained As bonds which are present in the α^2 -(2 × 4) unit cells or by using a different crystallographic face, such as the (110) surface.

III-V (110) surfaces are an appealing alternative to traditional (001) surfaces due to their lack of group V dimers and intrinsic surface defects. III-V (110) surfaces are devoid of metallic In-Ga bonds. Instead, the surface has III-V heterobonds (i.e., no homodimers), and the surface group III-V atoms are relaxed, i.e., buckled, leaving the As atoms with filled dangling bonds in a near-tetrahedral sp^3 geometry and the group III atoms with empty dangling bonds in a nearplanar sp^2 geometry. The relaxed bonding structure results in the dangling bonds having electronic states outside of the bandgap⁷ and the Fermi level of the clean surface being unpinned.

The implementation of tri-gate transistors into commercial logic chips⁸ also increases the importance of III-V (110) surface passivation. The main benefits of using a fin based architecture are the reduction of short channel effects, minimized subthreshold swing, and a higher transconductance due to better electrostatic confinement.⁹ The (110) surface would be the dominant surface of vertically aligned III-V (001) based finFETs¹⁰, and with proper passivation this surface may lead to an ideal interface with the gate oxide.

In this study, the deposition of trimethylaluminum (TMA) was investigated as the Al_2O_3 seed layer on the GaAs (110) surface. While future finFETs will likely be fabricated with an InGaAs channel, GaAs was used as a model to simplify defect-free sample preparation, data interpretation, and density functional theory (DFT) modeling. Furthermore, GaAs has a wider bandgap than InGaAs so passivation techniques developed on GaAs are likely to also be effective on InGaAs. The effects of varying the dosing and the post deposition annealing (PDA) conditions upon the formation of a highly ordered monolayer with a high nucleation density were

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studied since nucleation of the gate oxide atomic layer deposition (ALD) in each unit cell is critical for a minimal equivalent oxide thickness (EOT). This is the first study which uses scanning tunneling microscopy/spectroscopy (STM/STS) to study the atomic bonding configuration and electronic structure of any ALD precursor on a semiconductor (110) surface. Since the TMA reaction on GaAs (110) results in formation of Al-Ga metallic bonds, dual passivation was investigated in which the TMA/GaAs (110) surface was dosed with H₂O or O₂. DFT calculations were performed to model the bonding configuration and density of states of the clean and TMA/oxidant deposited GaAs (110) surfaces.

II. EXPERIMENTAL

The samples were either n-type GaAs (001) wafers doped with 4×10^{18} cm⁻³ Si or InGaAs (110) with a dopant level of 1×10^{18} cm⁻³ Si on InP (110). The GaAs (001) wafers were loaded into the Omicron variable temperature UHV chamber with a base pressure of $<1 \times 10^{-10}$ torr in a custom built cross-sectional sample holder. Samples were cleaved in situ to expose the (110) crystallographic face and were transferred to the scanning probe microscopy (SPM) chamber, base pressure 2×10^{-11} torr, where STM and STS were performed. STM was used in constant current mode to determine the atomic configuration of the surface while STS was used in variablez mode to measure the electrical quality of the surface.^{2,11,12} The tunneling current set point was 0.1 nA, and the samples were biased at -2.5 V. The STS curves were taken while ramping the sample bias from -2.5 V to 2.5 V and simultaneously moving the tip toward then away from the surface. All STS curves shown are an average of eight individual curves. All adsorbate structures were reproduced and the bonding configuration observed via STM and electronic structure observed via STS at least twice.

STM/STS were performed on the clean GaAs (110) surface, subsequently 10-500 Langmuirs (L) of TMA were dosed at temperatures between 25 °C and 200 °C. The samples were annealed between 135 °C and 350 °C for 30 min. All samples were annealed in an ultra-high vacuum. STM was used to probe the atomic bonding structures of partial coverage and full coverage TMA surfaces. STS was used to determine Fermi level pinning of the TMA dosed surfaces. For the dual passivation studies on GaAs (110), following TMA deposition, between 1000 and 60 000 L of H₂O or O₂ were dosed at room temperature. A series of subsequent anneals were performed in 30 min increments at 250 °C. STM and STS were performed to observe the bonding configuration and electrical characteristics of the surface after both the TMA and the oxidant were dosed. The amounts of TMA and oxidant dosed in these experiments are generally smaller than typical ALD doses by about an order of magnitude. Auger electron spectroscopy or x-ray photoelectron spectroscopy studies were not performed on GaAs(110) since the electron/x-ray beam spot size for either instrument is larger than the exposed (110) surface.

MBE grown InGaAs (110) wafers with a dopant level of 1×10^{18} cm⁻³ Si on InP (110) substrate were used to determine the presence of Al on the surface with XPS. 50 L

of TMA was initially dosed at 200 °C followed by a PDA at 230 °C for 30 min. Using a home-built pulsed valve system, 5 cycles of TMA/H₂O were subsequently deposited. The ALD consisted of 3 s stabilization step for TMA, followed by a 10 s TMA pulse/pump step in which the sample was exposed to the entire dose volume. The H₂O step was identical to the TMA step but with a 5 s stabilization step. The pulse lengths in this system were long due to the low vapor pressure of the precursors and the walls of the system being at 25 °C. Five additional ALD cycles were used for STS measurements of the bandgap of the a-Al₂O₃.

An *in situ* monochromatic XPS (XM 1000 MkII/SPHERA, Omicron Nanotechnology) was used to determine the presence of Al and O on the InGaAs (110) surface. The XPS was operated in constant analyzer energy mode with a pass energy of 50 eV and the line width of 0.1 eV using an Al K α source (1486.7 eV). The takeoff angle was 30° relative the surface with an acceptance angle of 7°. CASA XPS v.2.3 was used to analyze the data. The relative intensities of the core-level peaks were quantified by calculating the peak area and diving by the relative sensitivity factors.

All DFT simulations were performed with the Vienna Ab-Initio Simulation Package (VASP)^{13,14} using projector augmented-wave (PAW) pseudopotentials (PP)¹⁵ and the PBE (Perdew-Burke-Ernzerhof) exchange-correlation functional.^{16,17} The choices of PBE functional and PAW PP were validated by parameterization runs demonstrating good reproducibility of experimental lattice constants, bulk moduli, and formation/cohesive energies for bulk crystalline GaAs.

III. RESULTS AND DISCUSSION

A. STM of TMA deposition on GaAs (110) surface

The cleaved GaAs (110) surface has been well studied with STM.¹⁸⁻²¹ STM was initially employed in this study to ensure the surface was free of contaminants and defects; Fig. 1(a) shows a filled state $10 \times 10 \text{ nm}^2$ STM image of the clean GaAs (110) surface. The crystallographic directions are slightly tilted due to drift in the piezo in the scanner; this is an inherent problem which is observed in several of the images. The rows oriented in the $(\bar{1}10)$ direction are comprised of a zigzag chain of Ga and As atoms with heterobonds; this chain is depicted in a model of the clean surface shown in Fig. 1(b). The GaAs (110) zigzag chain is buckled so that each surface As atom is elevated relative to each surface Ga atom^{22,23} because the filled dangling bonds on the As atoms induce near tetrahedral (sp³) bonding angles, while the empty dangling bonds on the Ga atoms allow near planar (sp²) bonding angles. The filled dangling bonds on the As atoms are directly observed in filled state STM images.

Initially, 5 L of TMA was dosed at 25 °C followed by an anneal at 135 °C for 30 min to obtain partial coverage. As shown in Fig. 2, STM reveals regions of the clean surface (red circle) as well as regions that have reacted with TMA (blue box). The blue box contains two sites where it is hypothesized that two TMA molecules have dissociatively chemisorbed as dimethylaluminum (DMA) between the clean



FIG. 1. Clean GaAs (110). (a) A filled state STM image of the clean GaAs (110) surface. The filled dangling As bonds are directly observed resulting in rows oriented in the ($\overline{1}10$) direction. (b) A model of the clean GaAs (110) surface showing the filled As dangling bonds (filled ovals) and empty Ga dangling bonds (empty ovals) Notice the As-Ga rows are buckled which allows each As atom to be in a nearly sp³ geometry and each Ga to be in a nearly sp² geometry.

GaAs rows. Line traces indicate these reacted sites are 0.5 Å above the clean surface. A reaction between TMA and the surface has occurred, but a larger dose is necessary to achieve full coverage.

Exposure of the clean surface to 10 L of TMA at 25 °C and a subsequent anneal at 135 °C for 30 min resulted in the formation of \sim 1/3 of a monolayer (ML) of adsorbates. Ordered rows of chemisorbates formed which are rotated 40° clockwise relative to the clean surface rows, as shown in Fig. 3. The line trace in the inset in Fig. 3 shows the spacing between adjacent rows was 17 Å, 3× the spacing of the clean surface rows. A proposed qualitative model for low coverage TMA chemisorption is shown in Fig. 3(b). Three DMA molecules reacted with the surface in a stepwise manner, giving the appearance of diagonal rows. DFT was not used to



FIG. 2. Low coverage TMA/GaAs (110) STM image after 5 L TMA dose at 25 °C followed by a 135 °C anneal for 30 min. The clean surface rows are visible (red circle). Regions of TMA chemisorbates are also observed (blue box). The blue box shows two sites where DMA molecules have chemisorbed between adjacent GaAs rows. The reacted sites had a height of 0.5 Å. TMA is clearly reacting with the surface but a larger dose is necessary to obtain full coverage

quantitatively model this system due to the size of the unit cell. For full passivation, it is necessary to increase this nucleation density while maintaining surface order.

Exposure of the clean surface to 50 L of TMA at 200 °C followed by an anneal at 230 °C for 30 min resulted in formation of an ordered monolayer of DMA with some defect sites. Figure 4(a) shows the ordered rows are oriented in the $(\bar{1}10)$ direction. The spacing between adjacent rows was measured to be 5.6 Å (see insert) which is identical to the spacing of the clean surface rows indicating the maximum nucleation density has been achieved.²³ A model for the full coverage chemisorption of TMA is shown in Fig. 4(b). It is proposed that TMA loses a methyl group, and the resulting dimethylaluminum (DMA) makes one Al-As bond and one Al-Ga bond. This is the likely bonding geometry since bonding between adjacent As or Ga row atoms is not possible without each atom making five total bonds, which is likely energetically unfavorable.²⁴ The full coverage DMA surface has three different reacted sites. The pink circle in Fig. 4(a) shows a dim site where DMA has bonded in the ideal configuration with rows oriented in the $(\bar{1}10)$ direction; this is the predominant chemisorption site and is modeled below with DFT to confirm the assignment. The yellow boxes show dim diagonal sites. The rows at these sites appear rotated 40° relative to the $(\bar{1}10)$ direction. These diagonal sites are believed to be DMA bonded between adjacent clean surface rows in a stepwise fashion giving the appearance of a diagonal row, similar to the low coverage case. The diagonal sites are never observed on the clean GaAs (110) surface. The diagonal sites are the same height as the vertical rows consistent with having nearly a full monolayer of DMA. It is noted that diagonal sites are not observed after large TMA doses (500 L). The blue triangle indicates a bright site on the full coverage



FIG. 3. Medium coverage TMA/GaAs (110). (a) STM image after 10 L dose of TMA at 25 °C followed by an anneal at 135 °C for 30 min. Rows are observed rotated 40° clockwise relative to the clean surface rows. Spacing between adjacent rows is 17 Å as shown in the line trace. (b) Proposed model for low coverage TMA chemisorption on GaAs (110). TMA dissociatively chemisorbs as DMA in a stepwise fashion giving the appearance in STM of a row (orange rectangle) that is rotated 40° clockwise relative to the clean surface rows.

surface. These are hypothesized to be AIO_x sites that form when background water in the dosing chamber reacts with the freshly deposited DMA monolayer. H₂O was not intentionally introduced into the system during this experiment. It is believed that water dissociatively chemisorbs between adjacent Al atoms and a TMA molecule subsequently chemisorbs onto the bridge bonding O atom. The height of these bright sites is 2 Å and two models have been proposed to explain these features (see below).

An annealing study was performed to determine the characteristics of DMA chemisorption on the clean GaAs (110) surface. After 500 L of TMA was dosed at 250 °C and subsequently annealed to 260 °C for 30 min, two different ordered regions appear, shown in Fig. 5(a). The blue arrow indicates regions of highly ordered rows with 5.6 Å spacing between adjacent rows, similar to the ideal bonding configuration in Fig. 4(a). The red arrow in Fig. 5(a) indicates regions with 11 Å spacing between adjacent rows, $2 \times$ the spacing of the clean surface which is not observed in the ideal TMA terminated



FIG. 4. High coverage TMA/GaAs (110) (a) An STM image of a 50 L dose of TMA at 200 °C followed by an anneal at 230 °C for 30 min. A complete monolayer of DMA is formed. Ordered rows of DMA (pink circle) are formed with an average of 5.6 Å between rows. This indicates that nearly maximum nucleation density has been achieved. Diagonal sites (yellow box) are observed and are attributed to two DMA molecules chemisorbing in a stepwise fashion, similar to the low coverage case. Bright sites (blue triangle) are believed to be AIO_x . (b) A model for the chemisorption of TMA on the GaAs (110) surface. Each TMA loses a methyl and bonds between adjacent GaAs clean rows forming an Al-Ga bond and an Al-As bond.

surface shown in Fig. 4(a). The hemispherical bright sites (green circle), believed to be AlO_x , initially average 2.5 Å in diameter. The same sample was subsequently annealed to 300 °C for an additional 60 min, shown in Fig. 5(b). The red box highlights regions of clean GaAs (110) that have been exposed by annealing; additionally, the AlO_x clusters have grown wider and taller with an average diameter of 3.5 Å. This suggests after annealing to 300 °C the bright sites (green circle) coalesce and this results in regions of TMA-free clean GaAs (110). There are also dim reacted sites (yellow triangle) that remain on the surface which are likely DMA or MMA molecules that have not desorbed. A small amount of vertical ordering remains, but the nucleation density has dramatically decreased. A final anneal to 350 °C for 60 min was performed, Fig. 5(c), and the AlO_x clusters grew to an average diameter of 6 Å and larger regions of the clean surface became exposed, as seen in the red box in Fig. 5(c). A few dim sites remain indicating sites where DMA molecules have remained in their initial chemisorption sites, but no vertical ordering is evident. There is a large thermodynamic driving force to form Al-O bonds (511 kJ/mol), and when the sample is heated, the O atoms diffuse on the surface and form highly stable clusters of AlOx.²⁵ This set of experiments demonstrates that the TMA bonding is relatively weak and does not perturb the bonds



FIG. 5. Effect of anneal temperature after high TMA dose on GaAs(110). (a) STM image of 500 L TMA dose at 250 °C with subsequent anneal at 260 °C for 30 min. The blue arrow indicates regions with 5.6 Å spacing between adjacent rows which is observed for the full coverage surface. The red arrow indicates regions with 11 Å spacing between adjacent rows corresponding to a decreased nucleation density. There are bright sites (green circle) which are believed to be AlO_x and initially average 2.5 Å in diameter. (b) STM image of the same sample annealed to 300 °C for 60 min. Areas of clean surface (red box) are visible as well as formation of large white adsorbate clusters (green circle). It is hypothesized that AlO_x clusters are coalescing which results in the larger bright sites and a larger area of exposed clean surface. (c) Same sample annealed to 350 °C for 60 min. Larger areas of clean surface are visible (red box) and bright clusters continue to coalesce (green circle) with average diameters of 6 Å. DMA molecules which have remained in their initial chemisorption sites (yellow triangle) are also visible.

within the substrate, but any oxygen present on the surface will react with Al and cluster at temperatures above 200 °C.

Figure 6 shows a STM image obtained after dosing the full coverage DMA/GaAs (110) surface with 1000 L of O_2 at 25 °C followed by an anneal at 230 °C for 30 min and a subsequent anneal at 250 °C for 60 min. Ordered rows are visible in the ($\bar{1}10$) direction (blue lines) indicating that after oxidant dosing the surface order is maintained. The dark sites (green box) are hypothesized to be sites in which a DMA molecule has been scavenged by oxygen resulting in exposure of the clean surface while the bright sites (red arrow) are believed to be sites that have reacted with more than one -O- atom



FIG. 6. STM of O₂/TMA/GaAs (110). Filled state STM image of the DMA/GaAs (110) surface dosed with 1000 L of O₂ at 25 °C followed by an anneal at 230 °C for 30 min and subsequently 250 °C for 1 h. Ordered rows are visible (blue lines) in the ($\bar{1}10$) direction indicating the surface order is maintained after dosing O₂. The dark sites (green square) are hypothesized to be sites in which oxygen has scavenged a DMA molecule exposing the clean surface while the bright sites (red arrow) are hypothesized to be sites that have reacted with more than one O atom resulting in a site protruding from the surface.

resulting in a site that is protruding from the surface, hence appearing bright in STM.

B. STS of TMA deposition on GaAs (110) surface

STS probes the local density of states (LDOS) of the surface.¹¹ Experiments were only performed with n-type GaAs (110) since Fermi level pining results in a Fermi level position slightly below midgap²⁶ independent of n vs. p doping thereby making only measurement on n-type samples fully diagnostic.

Figure 7 compares the STS spectra of the clean GaAs (110) surface and full coverage DMA surface. The clean surface (black curve) Fermi Level (E_f), which is defined as the 0 V position, is located about 0.4 V from the CB edge, consistent with an unpinned E_f .²⁰ The full coverage DMA surface (blue curve) shows the E_f has shifted (red arrow) and is now about 1.0 V from the CB edge, indicative of surface



FIG. 7. STS spectra of the clean surface (black) and full coverage TMA surface (blue). The E_f for the clean surface is located near the CB indicating an unpinned surface. The full coverage surface has a large CB edge state starting at 0.5 V and the E_f has shifted to midgap indicating the surface is pinned.



FIG. 8. STS comparison of full coverage TMA surface (blue). Notice large CB edge state starting at 0.5 V. This sample was subsequently dosed with 1000 L O₂ at 25 °C and annealed to 250 °C for 30 min (red). The CB edge state is reduced by about $3\times$. The same sample was dosed with an additional 59 000 L of O₂ at 25 °C with an anneal at 250 °C for 30 min (olive). The CB edge state is further reduced but still not completely passivated. A separate experiment was performed where 2000 L of H₂O was dosed at 25 °C followed by an anneal at 250 °C for 30 min on full coverage TMA surface (black). Notice the CB edge state is completely suppressed indicating selective insertion of the oxidant into the metallic Al-Ga bonds.

pinning. Additionally, a large CB edge state is observed starting at ~ 0.5 V. This data indicates that a highly ordered monolayer of DMA on the (110) surface pins the Fermi level near midgap consistent with DFT calculations which suggest the CB edge state is a result of Al-Ga bond formation.

STS was performed on the oxidant dosed DMA/GaAs surface. Figure 8 compares the full coverage TMA surface (blue curve) with O₂ or H₂O dosed surfaces. The CB edge state is dramatically reduced after dosing the DMA surface with 1000 L of O₂ at 25 °C followed by an anneal at 250 °C for 30 min (red curve) consistent with the hypothesis that O has inserted into the Al-Ga metallic bonds. A small CB edge states remains, indicating not all of the metallic bonds have been passivated. A subsequent 59 000 L dose of O_2 at 25 °C with an anneal at 250 °C for 30 min (olive curve) did not remove the remaining CB edge states, but it slightly shifted the E_f toward the CB consistent with further passivation. In a separate experiment, 2000 L of H₂O was dosed onto the DMA/GaAs (110) surface at 25 °C with a subsequent anneal at 250 °C for 30 min (black curve), and the CB edge states were completely passivated. It is hypothesized that the water dissociates and the -OH groups preferentially insert between the Al-Ga metallic bonds, similar to the –O–insertion, consistent with the DFT calculations below.

Since it was not possible to confirm the presence of aluminum on the cleaved GaAs (110) surface, MBE grown In-GaAs (110) samples were employed to confirm a complete monolayer of DMA chemisorbs to the surface. STS was performed of the InGaAs (110) TMA/H₂O dosed surface to ensure correlation with the TMA/H₂O dosed GaAs (110) results. Figure 9 compares three STS curves. The clean InGaAs (110) surface (blue) has a bandgap of about 0.8 eV. After dosing



FIG. 9. STS spectra of clean InGaAs (110) vs. TMA/H₂O dosed surface. (Blue) Clean InGaAs (110) showing bandgap of 0.8 eV. Sample was subsequently dosed with 50 L of TMA at 200 °C and annealed at 230 °C for 30 min. After the initial TMA deposition Al_2O_3 was deposited in 5 ALD cycles (blue curve). The bandgap has increased to 2 eV. An additional 5 cycles of ALD were performed (red curve) and the bandgap further increased to 2.94 eV indicating a high nucleation density of the initial TMA deposition.

50 L of TMA at 200 °C followed by an anneal at 230 °C for 30 min and 5 subsequent cycles of Al₂O₃ ALD (green curve) the bandgap increased to 2 eV. About 30 STS spectra were taken at three different locations on the sample to ensure sample uniformity across a range of surface sites. After 10 cycles of Al₂O₃ ALD the band gap increases to 2.94 ± 0.25 eV. The bandgap increasing to that of a thin amorphous film of Al₂O₃ after 10 cycles is consistent with having an ordered monolayer of DMA with a high nucleation density on the InGaAs (110) surface which serves as the template for ALD of Al₂O₃.²⁷

XPS was performed on the sample which had 10 ALD cycles, and it was found that the ratio of Al to O was 0.65.²⁴ This ideal stoichiometry also is consistent with having a very good nucleation density which allows for uniform oxide deposition.

C. Density functional theory simulations

Figure 10 shows a side view of DFT models and the calculated density of states (DOS) for (a) clean GaAs (110), (b) full coverage DMA, (c) –OH, and (d) –O– passivated full coverage TMA surfaces. The clean surface (a) has the buckled GaAs zigzag chains and the DOS shows a clean bandgap. This is consistent with experimental data showing the clean surface has an unpinned Fermi level. The full coverage DMA model (b) shows each Al atom bonding to an As atom and a Ga atom. The DOS shows a large conduction band (CB) edge state which is attributed to the chemisorption of TMA resulting in a metallic Al-Ga bond (red arrow). This supports the proposed model in Fig. 3 for DMA chemisorption in which each Al atom will make an Al-As bond and an Al-Ga bond. Experimentally, the CB edge state is observed consistent with the presence of the metal-metal bonds pinning the E_{f} midgap. The DFT calculated DOS shows that by inserting an -OHgroup (c) into the metallic Al-Ga bond the CB edge state is fully passivated. This insertion eliminates any metallic bond



FIG. 10. DFT model of the clean and reacted GaAs (110) surface. DFT model (left) and calculated DOS (right) of (a) clean GaAs (110) surface. The DOS shows no gap states which was experimentally verified using STS which showed the clean surface had an unpinned E_f . (b) The full coverage DMA surface. Notice the Al-Ga bond (red arrow) which induces a CB edge state starting at 0.5 (eV). Experimentally, this CB edge state is observed and pins the E_f midgap. (c) Model and DOS for –OH passivated DMA surface. –OH groups (red) inserted between Al-Ga bond which eliminated the CB edge state. (d) Model and DOS for –OH passivated full coverage DMA surface. Notice similarities between electronic structures of (c) and (d).

character and restores the DOS to that of the clean surface. In (d), oxygen was inserted and -O-atoms bonded between the metallic Al-Ga bond and the CB edge states were suppressed. This is a result of oxidizing the metallic bond and should result in an unpinned surface E_f . In (d), one of the methyl groups from DMA has bonded to the O atom, but the DOS shows this does not have a significant effect on the electronic structure.

Figure 11 shows two different models for the bright sites observed in Fig. 4(a). It is proposed that in each model DMA forms a monolayer as discussed above, after formation of the initial monolayer a background H₂O or O₂ molecule dissociatively chemisorbs between (a) two DMA molecules along the GaAs (110) row direction or (b) between DMA molecules that are bonded to adjacent GaAs (110) rows. Subsequently, an additional DMA molecule from TMA was placed onto the bridging O atom since the experiments were performed with excess TMA. Note the models in Fig. 10 show two adjacent defect sites. The bright sites in Fig. 4(a) are believed to consist of only one defect site, but the double defect sites were modeled to be sure the defects do not cross react. These models result in defect sites which are about 2 Å taller than the DMA only sites. The height difference is what causes the defects to appear bright in the STM image in Fig. 4(a). Model (a) shows a TMA molecule as a volatile reaction product consistent with TMA having weak bonding to the bridging O atoms in part due to steric hindrance. In contrast, model (b) has C_2H_4 and H₂ as volatile reaction products consistent with DMA having ligands which readily desorb. The total energy for each system was calculated and model (a) had a total energy of -2.59 eV lower (i.e., more stable) than model (b). Since model (a) is the most thermodynamically favorable structure and it is expected that this site would appear bright in Fig. 4(a) because they are about 2 Å taller than a DMA only site, this is assigned as the structure for the bright defects in Fig. 4(a).



FIG. 11. Side views of DFT models of the bright defect sites on the full coverage DMA/GaAs (110) surface. (a) has an O atom bridge bonding between DMA molecules along the GaAs (110) row direction and a DMA molecule bonding on top of the O atom. This model has TMA as a volatile reaction product. (b) shows the O atom bridge bonding between DMA molecules in adjacent GaAs (110) rows with an additional DMA bonding to the O atom. This model has C_2H_4 and H_2 as volatile reaction products. Model (a) is 2.59 eV more stable than model (b).

IV. CONCLUSION

A defect-free GaAs (110) surface has been employed to nucleate the ALD of Al₂O₃ in every unit cell while maintaining a highly ordered smooth surface. Passivation of III-V (110) surfaces is especially challenging since the surfaces are dominated by heterobonds so a precursor will make bonds to both the group III and group V atoms potentially pinning the Fermi level. It was proposed that TMA dissociatively chemisorbs to the surface, making one Al-As bond and one Al-Ga bond. DFT was used to model this system and the calculated DOS show a large CB edge state which was caused by chemisorption of TMA on the surface resulting in formation of a metal-metal bond. To passivate this CB state -OH and -O- groups were inserted into the metallic bonds on the surface; in the DFT model this completely suppressed the CB edge state. Experimental work verified the theoretical work and it was shown that by starting with a clean GaAs (110) surface, it is possible to form an ordered monolayer of TMA. STS was used to verify that the TMA monolayer has a large CB edge state. By utilizing a dual passivation scheme where the TMA surface was dosed with either O₂ or H₂O this state was suppressed due to elimination of the metal-metal bonds.

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