Scanning tunneling microscopy/spectroscopy study of atomic and electronic structures of In_2O on InAs and $In_{0.53}Ga_{0.47}As(001)-(4\times 2)$ surfaces

Jian Shen,^{1,2,a)} Evgueni A. Chagarov,² Darby L. Feldwinn,² Wilhelm Melitz,^{1,2} Nancy M. Santagata,² Andrew C. Kummel,^{2,b)} Ravi Droopad,³ and Matthias Passlack⁴ ¹Materials Science and Engineering Program, University of California, San Diego, La Jolla, California 92093, USA ²Department of Chemistry and Biochemistry, University of California, San Diego, La Jolla, California 92093, USA ³Department of Physics, Texas State University, San Marcos, Texas 78666, USA ⁴Taiwan Semiconductor Manufacturing Company, Ltd., Europe BV, Kapeldreef 75, 3001 Leuven, Belgium

(Received 13 June 2010; accepted 10 September 2010; published online 26 October 2010)

Interfacial bonding geometry and electronic structures of In₂O on InAs and $In_{0.53}Ga_{0.47}As(001)-(4 \times 2)$ have been investigated by scanning tunneling microscopy/scanning tunneling spectroscopy (STM/STS). STM images show that the In₂O forms an ordered monolayer on both InAs and InGaAs surfaces. In₂O deposition on the InAs(001)- (4×2) surface does not displace any surface atoms during both room temperature deposition and postdeposition annealing. Oxygen atoms from In₂O molecules bond with trough In/Ga atoms on the surface to form a new layer of O-In/Ga bonds, which restore many of the strained trough In/Ga atoms into more bulklike tetrahedral sp^3 bonding environments. STS reveals that for both p-type and n-type clean $In_{0.53}Ga_{0.47}As(001)-(4 \times 2)$ surfaces, the Fermi level resides near the valence band maximum (VBM); however, after In₂O deposition and postdeposition annealings, the Fermi level position is close to the VBM for *p*-type samples and close to the conduction band minimum for *n*-type samples. This result indicates that In₂O bonding eliminates surface states within the bandgap and forms an unpinned interface when bonding with $In_{0.53}Ga_{0.47}As/InP(001)-(4 \times 2)$. Density function theory is used to confirm the experimental finding. © 2010 American Institute of Physics. [doi:10.1063/1.3497040]

I. INTRODUCTION

III-V compound semiconductors are known as potential channel materials for metal-oxide-semiconductor field-effect transistors (MOSFETs). III-V MOSFETs could increase intrinsic device speed due to their 50 times greater low field mobility than silicon.¹⁻³ However, these III–V channel materials have not been used in real MOSFET devices due to their poor native oxide quality. The key to fabricating a practical III-V MOSFET is forming an unpinned oxide/ semiconductor interface with low fixed charge and low trap density.⁴ On an atomic level, electronic defects result from strong perturbations to the electronic structure of the oxide/ semiconductor interface forming interface trap states. These perturbations can be caused by formation of localized charges, interface dipoles, or dangling bonds, which accompany oxide/semiconductor chemical bonding. It is critical to investigate and understand the oxide/semiconductor interfacial bonding geometries and electronic structure in order to determine the causes of the Fermi level pinning and obtain a fundamental understanding of surface passivation of III-V compound semiconductor.

InAs and InGaAs are attractive channel materials for high speed, low power MOSFETs due to their very high intrinsic electronic mobility ($\sim 4 \times 10^4$ and $1 \times 10^4 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ compared to Si (~ 1.5) $\times 10^3$ cm² V⁻¹ s⁻¹) at 300 K.^{5,6} A few InAs based FETs (Refs. 2 and 7) and many InGaAs based MOSFETs (Refs. 8-11) structures have previously demonstrated potential for high performance III-V MOSFET devices. Although InAs(001) (Refs. 12-15) has been the focus of many scanning tunneling microscopy (STM) and x-ray photoelectron spectroscopy (XPS) studies, very few STM and XPS studies have been performed on In_{0.53}Ga_{0.47}As(001).¹⁶⁻¹⁸ Furthermore, only one STM study has been performed on atomic bonding geometry of oxide/InAs or InGaAs(001) interfaces.¹⁹ The current paper focuses on the oxide bonding to the group III-rich (4×2) reconstruction of InAs and In-GaAs(001) surface. The group V As-rich reconstruction is likely to undergo oxygen induced displacement reactions when bonding to oxides because the dimerized arsenic atoms are likely to react with any ambient O₂ during oxide deposition thereby pinning the Fermi level directly or indirectly.^{20–23} Conversely, the group III-rich reconstructions are less reactive to O₂ and, therefore, are probably quite suitable for oxide deposition.²⁴

In this paper, the bonding geometries along with electronic structures of In_2O on InAs and $In_{0.53}Ga_{0.47}As(001)$ -(4×2) are reported. STM is used to determine the exact interfacial bonding geometries of the $In_2O/InAs$ and $In_{0.53}Ga_{0.47}As(001)$ -(4×2) after room tem-

133, 164704-1

^{a)}Electronic mail: jimshen@ucsd.edu.

^{b)}Electronic mail: akummel@ucsd.edu.

perature oxide deposition. In addition, the effects of postdeposition annealing on In₂O bonding on InAs surface are investigated. Scanning tunneling spectroscopy (STS) is performed on clean and oxide deposited $In_2O/In_{0.53}Ga_{0.47}As(001)-(4 \times 2)$ interfaces to investigate the electronic structures and determine the Fermi level pinning for this surface since the bandgap of $In_{0.53}Ga_{0.47}As$ is 0.74 eV, while the bandgap of InAs is only 0.35 eV, which makes STS very challenging on InAs surface. Density functional theory (DFT) simulation is used to model the bonding structures that are observed by STM so that the cause of the Fermi level pinning and unpinning can be determined.

II. EXPERIMENTAL AND COMPUTATIONAL METHODS

Experiments are performed in two ultrahigh vacuum (UHV) chamber systems equipped with low energy electron diffraction (LEED) and either a Park Scientific room temperature (RT) or an Omicron variable temperature (VT) STM. STM measurements are carried out at room temperature using electrochemically etched tungsten tips. Images taken in the Park Scientific RT-STM system are labeled in the text and the figure captions as *Park Scientific*. Molecular beam epitaxy is employed to grow 0.2 μ m of either $1\times10^{18}~{\rm cm^{-3}}$ doped InAs on InAs(001)1 $\times10^{18}~{\rm cm^{-3}}$ doped substrates or 1×10^{18} cm⁻³ doped In_{0.53}Ga_{0.47}As on lattice-matched InP(001) 1×10^{18} cm⁻³ doped substrates. Both *p*-type and *n*-type samples are grown and capped in situ with 500 Å of As₂ to prevent substrate reactions upon exposure to air. The wafers are transferred to a vacuum container for transporting to the STM chamber. Arsenic capped wafers are directly (Park Scientific system) or radiatively (Omicron system) heated to get (4×2) surface in the UHV preparation chamber.^{14,25} After the (4×2) surface reconstruction is verified by LEED, the sample is transferred to the STM chamber without breaking the vacuum.

STM and STS measurements are performed at room temperature using the constant current tunneling mode and the variable tip-sample separation methods. For the InAs surface, large size STM images can be recorded with stable tunneling due to the low density of surface defects; conversely, for the InGaAs surface, only small size STM images can be recorded with reasonable tip stability due to the high density of surface defects. Therefore, the different sizes of STM images were usually recorded for InAs and InGaAs in this study. The clean (4×2) surfaces can be observed with both filled and empty state STM imaging. Subsequently, indium oxide is deposited by evaporating sintered $In_2O_3(s)$ (Aldrich Chem. Co.) from a high temperature effusion cell (Applied EPI) contained in a differentially pumped chamber. $In_2O_3(s)$ sublimates as In_2O (g) and O_2 (g) at 1000–1025 °C.²⁶ However, due to the low sticking probability of O_2 on group III-rich (4 \times 2) surfaces,²⁴ the majority of the adsorbing species is In₂O. In the experiment, a thermocouple is used to measure the sample temperature. The thermocouple is positioned on the sample manipulator, not on the sample, since the sample must be wireless for transfer from the manipulator to the STM stage. Since the thermocouple does not directly touch the sample, the accuracy of the temperature measurement is in the range of ± 20 °C. Therefore, no difference is observed when an extra 10-20 °C postdeposition annealing is applied.

All DFT simulations are performed with the VIENNA AB INITIO SIMULATION PACKAGE (VASP) (Refs. 27 and 28) using projector augmented-wave (PAW) pseudopotentials (PP) (Refs. 29 and 30) and Perdew-Burke-Ernzerhof (PBE) exchange-correlation functional.^{31,32} The choice of PBE functional and PAW PP's is validated by parametrization runs demonstrating good reproducibility of experimental lattice constants, bulk moduli, and formation energies for bulk crystalline InAs and GaAs. A Brillouin zone integration is performed at $4 \times 4 \times 1$ Monkhorst–Pack k-point mesh and a plane wave energy cut-off of 400 eV. A double (4×2) reconstructed unit cell is used consisting of seven atomic layers with a (001) surface orientation. The bottom layer As atoms are passivated by H atoms with fractional 3/4 |e| charge to mimic a continuous InGaAs and InAs bulk according to Ref. 33. The slabs are relaxed using conjugate-gradient relaxation algorithms with a 0.05 eV/Å force tolerance level. During relaxation, the three bottom layers are fixed in their bulk positions. The vacuum layer over ~ 15 Å is added over the slabs to eliminate spurious interaction through periodic boundary conditions (PBCs). To compensate for the spurious electric field induced by PBCs for this type of system, a dipole correction is applied.^{27,28,34} For the $In_{0.5}Ga_{0.5}As$ slab, a bulk unit cell is formed by altering a GaAs unit cell by substituting half of Ga atoms with In atoms following a checkerboard pattern and using DFT to optimize the lattice constant of the alloy to equilibrium value. All slab total energies are reported per double (4×2) unit cell. The reference state for the clean surface is the lowest energy structure as calculated by DFT. This structure has undimerized row atoms and highly buckled group III dimers in the trough, not observed experimentally probably due to defects and limited terrace size; however, it is employed as the reference state since the lowest energy structure must be used for all thermodynamic calculations of chemisorption binding energy.^{14,25}

III. EXPERIMENTAL RESULTS

A. $InAs(001)-(4 \times 2)$ surface

Figure 1 shows filled state VT-STM and empty state STM images of the In-rich InAs(001)-(4×2) clean surface along with a structure model illustrating the surface reconstruction. The InAs(001)-(4×2) surface consists of top In rows separated by 17 Å. These In rows have dicoordinated sp hybridized In atoms forming π bonds with tricoordinated As atoms at the edge of the row.^{14,25} Between the In rows are trough regions that contain two In–In dimers in each (4×2) unit cell [this unit cell is highlighted by a rectangle in Fig. 1(c)]. Details of the InAs(001)-(4×2) clean surface structure are discussed elsewhere.¹⁴

After the InAs(001)-(4×2) surface reconstruction is identified, In₂O molecules are deposited onto the room temperature InAs clean surface to study the oxide bonding. STM images of In₂O/InAs(001)-(4×2) surface are shown in Fig. 2 along with a structural model, illustrating the possible ox-



FIG. 1. (a) A filled state (V_s =-1.6 V, I_t =0.2 nA, and 100 Å×100 Å) STM images of InAs(001)-(4×2) clean surface. (b) An empty state (V_s =2 V, I_t =0.2 nA, and 100 Å×100 Å) STM images of InAs(001)-(4×2) clean surface. (c) An undimerized atomic structure model (Ref. 14) for InAs(001)-(4×2) reconstruction based on that originally proposed in Refs. 12 and 13. The green rectangle presents a unit cell of (4×2). Note that the empty state image is taken in the Park Scientific RT-STM system and In atoms on the row are undimerized and at the same height with As atoms at the edge of row.

ide bonding structure for room temperature deposition. It is assumed that In_2O does not dissociatively chemisorb because no O sites or In sites were observed on the surface. O₂ dissociatively chemisorbs into O atoms on InAs(001)-(4×2); the oxygen binding site is insertion into the In atoms on the rows in the [1 1 0] direction; in filled state STM images, the atomic oxygen is dark;²⁴ these dark sites were not observed for In₂O dosing of either InGaAs(001)-(4×2) or InAs(001)-(4×2). Excess indium on the III–V surface tends to form metallic droplets on the surface, which appear as



FIG. 2. (a) A filled state (V_s =-1.5 V, I_t =0.2 nA, and 520 Å×520 Å) STM image of the InAs(001)-(4×2) surface with ~25% coverage of In₂O. (b) Expanded STM image taken from the green box in (a). (c) An atomic bonding structure model for In₂O deposition on InAs(001)-(4×2) surface. (d) Line scanning profiles and atomic bonding structure diagrams of In₂O/InAs(001)-(4×2) surface along single In₂O chemisorption bonding sites perpendicular [-1 1 0] (top) and parallel [1 1 0] (bottom) directions, respectively. Note that this image is taken in the Park Scientific RT-STM system.

bright features in filled state STM image;³⁵ these bright cluster sites were not observed for In2O dosing of either InGaAs(001)- (4×2) or InAs(001)- (4×2) . A high resolution scan of a small region of the room temperature low coverage In₂O/InAs(001) surfaces reveals that the In₂O molecules only occupy single sites at the edge of the rows. These In₂O adsorbates most likely form new In-As bonds on the surface. The line scan profile in Fig. 2(d) along the $[1 \ 1 \ 0]$ direction shows the distance between the two bright In₂O sites is about 8.5 Å, which is identical to the repeat distance of the possible bonding sites proposed in Fig. 2(c). Note that this bonding site is just an empirical model and an exact bonding site is calculated using DFT as shown below. The empirical bonding site in Fig. 2(c) is a favorable bonding structure since As-O bond formation is avoided and no substrate atoms are displaced which tends to indirectly induce midgap states.^{4,22}

At medium coverage (25% of a monolayer), the In₂O adsorbates form islands that are elongated in the [1 1 0] direction as shown in Fig. 2(a). Prior to all the first layer sites being occupied with In₂O molecules, second layer growth is observed on the oxide islands. A height distribution analysis is performed to determine the room temperature growth mechanism. There is a bimodal height distribution.³⁶ The height between the oxide and clean surface is 1.5 Å, which is consistent with single monolayer growth according to the line scanning profile in the [-1 1 0] direction shown in Fig. 2(d). Each layer of oxide has the distinct heights corresponding to distinct layers of oxide. Layer by layer growth will be discussed in details elsewhere.³⁶ However, the second and subsequent layers appear to be amorphous since they do not form ordered structures in the x-y plane.

To form more ordered oxide structures, the effect of annealing $In_2O/InAs(001)-(4 \times 2)$ is studied. After postdeposition annealing, the oxide spreads out. As shown in Fig. 3(a), the annealed 390 °C surfaces are more ordered than the unannealed ones with respect to both island shape and the structure within the islands. The increased order after annealing is consistent with the lowest energy structure being an ordered first monolayer of oxide. The ordered structures contain oxide in the troughs with rows in the $\begin{bmatrix} -1 & 1 & 0 \end{bmatrix}$ direction. The distance between the ordered oxide rows is 8.5–13 Å in the $\begin{bmatrix} 1 & 1 & 0 \end{bmatrix}$ direction, which is close to two to three times the span of the InAs(001) bulk unit cell (4.3 Å). Before annealing, the oxide forms In-O-In-As bonds at the edge of row. After annealing, the In₂O overcomes kinetic barriers and O atoms from In₂O bond with In/Ga atoms in the trough to form new In₂O-In/Ga bonds. This change in bonding is responsible for the reduction in the major oxide height from 1.5 to 1 Å relative to the clean surface rows. A reduction in the multiple layers of oxides also occurs since the density of the brighter features is reduced after annealing. Most importantly, for both room temperature deposition and postdeposition annealing, the In₂O adsorbates never cause the displacements of any surface atoms on the InAs(001)- (4×2) surface. If the annealing temperature is raised above 450 °C using several cycles of annealing,³⁷ the In_2O molecules completely desorb, leaving behind the clean (4×2) surface, as shown in Fig. 3(b). The observations of ordered monolayer In₂O islands and desorption at around 450 °C are consistent with

Downloaded 26 Oct 2010 to 192.55.55.39. Redistribution subject to AIP license or copyright; see http://jcp.aip.org/about/rights_and_permissions



FIG. 3. Filled state (V_s=-1.5 V, I_t=0.2 nA, and 450 Å×450 Å) STM images of submonolayer In₂O deposited InAs(001)-(4×2) surface after postannealing at (a) 390 °C and (b) 450 °C. After 390 °C postdeposition annealing, the oxide is spread out, and the coverage increases from ~25% to ~45%. After 450 °C postposition annealing, all of the oxide is desorbed from InAs surface, leaving behind a clean (4×2) surface. Note that (b) is not taken from original clean InAs(001)-(4×2) surface; it is taken from oxide deposited surface after high temperature postdeposition annealing.

the In_2O forming weak covalent bonds, having attractive interactions between adsorbates, forming stronger bonding with the substrate than to itself, and not displacing any surface atoms.

For full monolayer coverage of $In_2O/InAs(001)-(4 \times 2)$ after postdeposition annealing at 380 °C, the oxide form large, well-ordered, flat terraces on the surface, as shown in Fig. 4. For the different coverage depositions, a fresh sample was used for each experiment. The identical surface cleaning process was applied to each sample to ensure that the clean surfaces are identical prior to oxide deposition. For comparison of with and without PDA, the same sample with oxide deposition was used. STM image shows that the surface is entirely covered by oxides, and the first oxide layer completely dominates on the surface. The step edge height is the same as on the clean surface (~ 3 Å) consistent with the theoretical one step edge value for InAs(001) surface (half a lattice constant, 1/2a=3.03 Å). In Fig. 4(b), a very small (4×2) surface region is visible where In rows run in the [1 1 0] direction, which confirms that the monolayer oxide



FIG. 4. (a) A filled state (V_s=-3 V, I_t=0.15 nA, and 1000 Å×1000 Å) STM image of the InAs(001)-(4×2) surface with almost 1 ML coverage of In₂O after postdeposition annealing at 380 °C. A fresh sample was used for full coverage deposition. (b) Expanded STM image (250 Å×250 Å) taken from the green box in (a). A small unreacted portion of the (4×2) clean surface is labeled as "A" in the STM image.

growth on InAs(001)-(4×2) surface has the same structure as the medium coverage surface. The oxides still form ordered rows in the $[-1\ 1\ 0]$ direction similar to the submonolayer coverage structures. At monolayer coverage, the distance between the oxide rows is predominantly 13 Å, but some distances between the oxide rows are around 8.5 Å. This can be rationalized by the 13 Å being a thermodynamically more stable structure due to strain. The monolayer coverage results indicate a low defect density on the clean InAs(001)-(4×2) surface,²⁵ and the stronger bonding of the oxide to InAs(001)-(4×2) than the oxide to itself facilitates surface oxide molecular diffusion to assist in the formation of an ordered flat first oxide layer.

B. In_{0.53}Ga_{0.47}As(001)-(4×2) surface

All of STM results show that the InAs surface has a low defect density and the annealed $In_2O/InAs(001)-(4 \times 2)$ surface is highly ordered. However, InAs has a small bandgap of only 0.35 eV, so it is difficult to study the electronic structure. Experiments were also performed on another III–V candidate $In_{0.53}Ga_{0.47}As$, which has a wider bandgap that facili-



FIG. 5. A filled state (V_s=-3 V, I_t=0.15 nA, and 600 Å×600 Å) STM image of the In_{0.53}Ga_{0.47}As(001)-(4×2) clean surface.

tates the electronic structure determination. A quantitative comparison of the $In_{0.53}Ga_{0.47}As(001)$ - (4×2) and InAs(001)- (4×2) shows the reconstructions are almost identical. Both surfaces have rows running in the [1 1 0] direction. The distance between the rows is ~17 Å. Between the rows are trough regions. However, $In_{0.53}Ga_{0.47}As(001)$ - (4×2) has at least a 4×higher surface defect density even on the best samples, and the charged defects observed by STM in the $In_{0.53}Ga_{0.47}As(001)$ - (4×2) surface.²⁵ Figure 5 is a typical large scale (600 Å×600 Å) STM image of the $In_{0.53}Ga_{0.47}As(001)$ - (4×2) clean surface.

A filled state STM image of low coverage In₂O without annealing on $In_{0.53}Ga_{0.47}As(001)\mbox{-}(4\mbox{-}2)$ is shown in Fig. 6(a). STM result reveals that the low coverage In₂O molecules mainly occupy single sites at the edge of the rows. Similar to $In_2O/InAs(001)-(4 \times 2)$, the In_2O molecules on $In_{0.53}Ga_{0.47}As(001)-(4 \times 2)$ most likely form new In-As bonds to the surface. Figure 6(b) shows a STM image of medium coverage In_2O on $In_{0.53}Ga_{0.47}As(001)-(4 \times 2)$ with postdeposition annealing at 380 °C. There are two types of bright features observed with STM. The intermediate bright feature (dark arrows) shows that the In₂O molecules fill the trough region between the group III In/Ga rows and form ordered structures along the rows in the $\begin{bmatrix} 1 & 1 & 0 \end{bmatrix}$ direction, which is different than on $InAs(001)-(4 \times 2)$ surface. The trough In₂O molecules are tightly packed with few missing sites. These relative long range ordered structures in the [1 1 0] direction may form preferentially on $In_{0.53}Ga_{0.47}As(001)-(4 \times 2)$ compared to $InAs(001)-(4 \times 2)$ due to the greater trough defect density on the clean $In_{0.53}Ga_{0.47}As(001)-(4\times 2)$ surface, which increases the binding energy of the trough sites, thereby increasing the barrier for diffusion within the trough or over the row. The oxide-oxide bonding is also stronger on $In_{0.53}Ga_{0.47}As(001)-(4 \times 2)$ surface than on the InAs(001)-(4×2) surface since a higher percentage of In_2O molecules bonds with the first layer In₂O; these second layer In₂O are the brighter features indicated by green arrows in Fig. 6(b); this is consistent with some In₂O molecules bonding to defect sites, thereby perturbing their electronic structure.



FIG. 6. (a) A filled state ($V_s = -2.2$ V, $I_t = 0.2$ nA, and 260 Å×260 Å) STM image of the $In_{0.53}Ga_{0.47}As(001)\mbox{-}(4\mbox{-}2)$ surface with low coverage of In₂O from room temperature deposition without annealing; the dark arrows show In₂O bonding sites for the first oxide monolayer growth. (b) A filled state (V_s =-2.5 V, I_t =0.2 nA, and 260 Å×260 Å) STM images of the $In_{0.53}Ga_{0.47}As(001)$ -(4×2) surface with a medium coverage of In_2O after postdeposition annealing (PDA) at 380 °C; the black arrows show the ordered first oxide layer structure along the rows in the [1 1 0] direction, and the green arrows show the second layer In2O molecules bonding with preexisting first layer In₂O in the trough. (c) A filled state ($V_s = -1.5$ V, I_t =0.2 nA, and 260 Å×260 Å) STM image of the InAs(001)-(4×2) surface with $\sim 25\%$ coverage of In₂O. (d) A filled state (V_s=-2.5 V, I_t =0.2 nA, and 260 Å \times 260 Å) STM image of the InAs(001)-(4 \times 2) surface with a medium coverage of In₂O after PDA at 380 °C. (e) An empirical atomic bonding structure model for In₂O deposition $In_{0.53}Ga_{0.47}As(001)-(4 \times 2)$ surface with top view and side view.

Similar to the In₂O/InAs case shown in Figs. 6(c) and 6(d), the In₂O/In_{0.53}Ga_{0.47}As bonding configuration is different before and after annealing. For both surfaces, after postdeposition annealing, the height difference between deposited oxide and surface In/Ga row is reduced from 1.5 to 1 Å. As shown in the DFT studies below, it is likely that the annealed In₂O no longer bonds with just the As atoms at the edge of row but also forms new O–In/Ga bonds, thereby lowering the height of the adsorbates. Figure 6(e) illustrates a possible bonding model of In₂O on In_{0.53}Ga_{0.47}As(001)-(4×2) surface. Note that this is an empirical bonding structure, and an exact bonding structure is calculated using DFT as shown below. For full coverage of In₂O/In_{0.53}Ga_{0.47}As(001)-(4×2) after postdeposition an-



FIG. 7. (a) A filled state (V_s =-2.5 V, I_t=0.25 nA, and 1000 Å × 1000 Å) STM image of the In_{0.53}Ga_{0.47}As(001)-(4×2) surface with almost 1 ML coverage of In₂O after postannealing at 380 °C. A fresh sample was used for full coverage deposition. (b) Expanded STM image (350 Å × 350 Å) taken from the green box in Fig. 8(a).

nealing at 380 °C, a filled state STM image is seen in Fig. 7, as well as an enlarged region. From this image, it is clear that the In₂O forms smooth ordered structure on In_{0.53}Ga_{0.47}As surface with a rms roughness of 0.9 Å, similar to full coverage of In₂O on InAs(001)-(4 × 2).

The electronic structure of the surface has been obtained by STS measurement. In STS, the tip is placed above the surface, and the tunneling current I(V) and the tunneling conductance dI/dV are simultaneously measured as a function of the applied dc voltage. The positive sample bias probes the empty density of states (DOS) distribution of the sample surface, and the negative sample bias probes the filled DOS distribution of the sample surface. The position of the band edges relative to 0 V (Fermi level) determines the electronic structure of the sample surface. In Figs. 8(a) and 8(b), blue curves show the STS spectra of the clean *p*-type and *n*-type $In_{0.53}Ga_{0.47}As(001)-(4 \times 2)$ surfaces. For clean unpinned samples, the Fermi level should reside near the valence band maximum (VBM) for *p*-type samples and near the conduction band minimum (CBM) for *n*-type samples. However, for both *p*-type and *n*-type $In_{0.53}Ga_{0.47}As(001)$ - (4×2) clean surfaces, the STS spectra show that the Fermi



FIG. 8. Scanning tunneling spectra for the $In_{0.53}Ga_{0.47}As(001)-(4 \times 2)$ clean surface and monolayer coverage of In_2O : (a) *p*-type sample and (b) *n*-type sample. For both *p*-type and *n*-type $In_{0.53}Ga_{0.47}As(001)-(4 \times 2)$ clean surfaces, the Fermi level (0 V) lies near the VBM. After oxide deposition and postannealing, for the *p*-type sample, the Fermi level remain near VBM (annealed at 380 °C); for the *n*-type sample, the Fermi level shifts to CBM (annealed at 380 °C). These results indicate that the Fermi level is unpinned after In_2O deposition. A 50 mV amplitude and 1.5 kHz sinusoidal modulation voltage are superimposed on the tip bias, and the dI/dV spectra is recorded using a DSP lock-in amplifier (Signal Recovery 7280)

level resides near the VBM. This Fermi level shift might be caused by surface band bending due to a surface dipole or surface states. DFT calculations show that the surface pinning is due to the strained unbuckled dimers in the trough of the 4×2 reconstruction. In Figs. 8(a) and 8(b), green curves show the STS spectra after full coverage In₂O deposition on *p*-type and *n*-type $In_{0.53}Ga_{0.47}As(001)-(4 \times 2)$ surfaces with postdeposition annealing at 380 °C. The STS spectra results show that after oxide deposition and postdeposition annealing, the Fermi level position remains near the VBM for *p*-type sample and is shifted to the CBM for *n*-type samples. Detained STS spectra on cleaved (110) surface of several III-V semiconductors has been performed by Feenstra showing the expected spectra for an unpinned surface.³⁸ The results prove that the deposition and 380 °C annealing of In₂O on $In_{0.53}Ga_{0.47}As(001)-(4 \times 2)$ unpin the interface because the Fermi level moves from the VBM toward the CBM for *n*-type samples. Note that the unpinned surface is not always obtained. The processing window for passivating the interface is very small. Only when the processing conditions are carefully selected and optimized as described above, the STS spectra results show that In₂O passivates the interface and InGaAs surface is unpinned.



FIG. 9. DFT relaxed atomic structures for group III-rich In_{0.5}Ga_{0.5}As(001) and InAs reconstructions with the DFT calculated total energy differences relative to the lowest total energy clean surface case (undimerizedbuckled). Note that all of InGaAs cases use the same substrate reference state. The InAs cases use two different substrate reference states since the single In₂O/InAs(001) (g) has a different substrate structure compared the double (h) and quadruple (i) $In_2O/InAs(001)$; the single site has undimerized atoms on the row and two buckled homodimers in the trough, while the double and quadruple sites have a row dimer and two one buckled homodimer in the trough.

● Ga ● In ● As ● O ○ H

IV. DENSITY FUNCTION THEORY RESULTS

A. Bonding structure

Based on experimental results, there are two potential simplified empirical bonding structures for In_2O on InAs and InGaAs surfaces: In–O–In–As site at the edge of row for low coverage without postdeposition annealing shown in Fig. 2(c) and In_2O –In/Ga site in the trough for intermediate or high coverage with postdeposition annealing shown in Fig. 6(c). Both bonding configurations have been modeled using the empirical model as the initial sites and allowing the DFT relaxation process to find the most stable bonding sites.

DFT calculation results of binding energy between oxide and surface show that the In-As edge site is less stable than the O-In/Ga trough site by about $\sim 0.81 \text{ eV}/\text{In}_2\text{O}$ for In-GaAs surface and ~ 0.77 eV/In₂O for InAs surface. Therefore, it is more energetically favorable for O atoms from In₂O molecules to bond over a trough dimer rather than just single In atoms from In₂O bonding to As atoms at the edge of the row. It is likely that only the In-O-In-As edge site is observed without postdeposition annealing because there is a kinetic barrier to In₂O-In/Ga bonding site formation. Calculations were performed for different oxide coverages to study the influence of In₂O coverage, including comparison between In₂O-In and In₂O-Ga bonding sites because experiments show that the In2O spontaneously forms monolayer islands, while most adsorbates show repulsion or threedimensional cluster formation. In Figs. 9(a)-9(c), In₂O-In

bonding configurations and total energy differences relative to clean surface for single, double, and quadruple In_2O molecules on double InGaAs-(4×2) unit cells are shown. The chemisorption binding energies for all In_2O sites on InGaAs(001)-

 (4×2) were calculated using the lowest energy clean surface structure since the $In_2O/InGaAs(001)-(4 \times 2)$ structures had a nearly identical structure to the lowest energy clean surface double unit cell: a single homodimer on the row and one highly buckled dimer in the trough. For $In_2O/InGaAs(001)-(4 \times 2)$, the In_2O-In chemisorption binding energies are nearly coverage independent, consistent with the absence of absorbate-absorbate repulsion. Figures 9(d)-9(f) show the In₂O-Ga bonding configuration with single, double, and quadruple In₂O molecules on double InGaAs- (4×2) unit cells. The In₂O–Ga chemisorption binding energies are also nearly coverage independent consistent with the absence of absorbate-absorbate repulsion. The results show that the In₂O-Ga bonding site is slightly more stable (0.2–0.3 eV/In₂O) than the In₂O–In bonding site. This is consistent with Ga atoms being more electronegative than In atoms, which enables Ga atoms to form slightly stronger bonds with O atoms than In atoms.

In₂O on InAs(001)-(4×2) with single, double, and quadruple In₂O sites are shown in Figs. 9(g)-9(i). The choice of reference sites is complicated because there are several nearly degenerate clean surface structures.¹⁴ For InAs cases,

two different substrate reference states are used since the single In_2O site on the InAs double unit cells case [Fig. 9(g)] has a different substrate structure, which has only undimerized row atoms and two highly buckled homodimers in the trough; conversely, the higher coverage sites [Figs. 9(h) and 9(i)] are nearly identical to the $In_2O/InGaAs(001)-(4 \times 2)$ sites with a single row homodimer and one highly buckled homodimer in the trough. Similar to the InGaAs(001)- (4×2) case, there is no repulsion between deposited oxide molecules on InAs(001)- (4×2) , which is consistent with experimental observations in the formation of flat ordered In₂O islands on group III-rich InAs surfaces. It is noted that the DFT shows that the high coverage bonding models are identical on InAs(001)- (4×2) and InGaAs(001)- (4×2) ; therefore, the differences observed in STM especially at intermediate coverage are interpreted to be consistent with differences in the kinetics of forming the island structures instead of differences in the bonding models.

B. Electronic structure

The spatial distribution of bandgap states shows that the mixed-buckled structure has pinning states localized at the strained unbuckled trough dimers and no pinning states on the row atoms, as shown in Fig. 10. This result is consistent with surface pinning of group III rich In_{0.5}Ga_{0.5}As(001)- (4×2) being caused by the strained unbuckled trough dimers and not by the row atoms. For the undimerizedbuckled structure, the buckling of the trough dimers relieves the stress and unpins the surface. Detailed reports of the surface pinning on InGaAs(001) can be found in Ref. 25. Figures 11(a)-11(d) show the electronic structures of full coverage In₂O on InGaAs(001)-(4 \times 2). To carefully show the bandgaps, the DOS Gaussian smearing parameter was set to sigma=0.1 eV (Fig. 11); smaller values of sigma create substantial noise in the calculated DOS curves. To ensure there are no small band edge or bandgap states obscured by the smearing parameter, the energy eigenvalues and the occupations for all K-points as well as just the gamma K-point were calculated and are shown in the supplementary material's Fig. 1.³⁹ The eigenvalues and occupancies did not reveal any band edge nor bandgap states that are absent from the DOS in Fig. 11.

Several nearly degenerate full coverage sites are modeled since some disorder is observed on the annealed surface. The DFT structures at full coverage show that there are at least four nearly energetically degenerate structures with only 0.06-0.31 eV/In2O binding energy difference range for the In₂O bonding on InGaAs surface. As previously discussed, most of the slight energy difference is due to differences in In₂O-Ga versus In₂O-In bonding. Figure 11 and Fig. 1 in the supplementary material also show the DOS of corresponding In₂O/InGaAs bonding structures.³⁹ The DOS for two mixed In₂O-In/In₂O-Ga bonding sites is unpinned since the bandgap is free of electronic states. For the In_2O-In only and In_2O-Ga only bonding sites, there are some bandgap states. Two clean InGaAs(001)- (4×2) surface structures are shown in Figs. 11(e) and 11(f) and Fig. 1 in the supplementary material along with their DFT calcu-



FIG. 10. The band-decomposed electron charge densities and Bader charge differences relative to in-bulk atoms of group III rich $In_{0.5}Ga_{0.5}As(001)$ for the mixed-buckled and undimerized-buckled. (a) The mixed-buckled structure with the charge density summed between -0.25 and +0.25 eV; the contour spacing is 5×10^{-3} eÅ⁻³. The charge density is in blue.

lated electronic structures. The group III dimers in the trough cause a large buckling in the lowest energy structure, which relieves stress [Fig. 11(f) and Fig. 1(f) in the supplementary material], but this structure is not observed experimentally either in STM or STS; for example, while the DFT DOS shows the interface as unpinned, the STS spectra in Fig. 8 shows the clean surface having an electronically pinned surface. All other surfaces contain at least one flat group III dimer in the trough. These highly strained atoms induce midgap states and pin the Fermi level [Fig. 11(e) and Fig. 1(e) in



FIG. 11. [(a)-(d)] O–In, mixed O–In/Ga, or O–Ga bonding structure with four In₂O molecules per double unit cell; the two models with mixed O–In/Ga bonding have no states in the bandgap. (e) Clean InGaAs surface with mixed undimerized and dimerized row structure. (f) Clean InGaAs surface with undimerized row and buckled trough dimer structure. Calculated corresponding DOS are displayed on the left side for each structure.

the supplementary material]. The STM/STS data and the DFT modeling are consistent with the deposition of oxide changing the trough bonding geometry and releasing the strain in unbuckled trough dimers, thereby unpinning the Fermi level of group III-rich InGaAs(001) surface. As shown in Figs. 11(a)-11(e) and Figs. 1(a)-1(e) in the supplementary material at full coverage, In₂O bonding restores about half the trough group III atoms to four-coordinate sp³ hybridized bonding, thereby eliminating the strain for these trough sites. For the mixed In₂O-In/In₂O-Ga bonding geometry, the DFT shows that the reduction in strain is sufficient to eliminate the midgap states. Since experimentally, the In₂O deposited InGaAs surface is not a completely ordered structure, the mixed In₂O-In/In₂O-Ga bonding geometry resembles more closely to the experimental results. O-Ga only bonding geometry is never expected for high coverage In2O deposition on InGaAs(001)-(4 \times 2) surface since the surface has a mixture of In and Ga atoms.

DFT electronic structure calculations are not reported for the oxide on InAs because standard DFT predicts a zero bandgap for bulk InAs and the DFT bandgap for InAs slab is a quantum confinement effect, which varies with oxide coverage. Accurate bandgaps can be calculated for InAs using hybrid functionals such as HSE06,^{40–43} but this technique is computationally expensive. Furthermore, it is difficult to compare DFT calculations of electronic structure of InAs to STS measurements since the bandgap of InAs is so small (0.36 eV) that the accuracy of STS of ± 0.1 eV is problematic. Therefore, in this study, DFT electronic structure calculations are reported only for InGaAs(001) and compared to STS measurements on this surface.

C. Oxides on GaAs, InAs, and InGaAs comparison

The bonding of In_2O on group III-rich InGaAs(001)-(4×2) is quite distinct from the bonding of O_2 , In_2O , and Ga_2O on the As-rich GaAs(001)-(2×4) surfaces.^{4,22,26} For O_2 chemisorption on GaAs(001)-(2×4), two O atoms break the As dimer bond and displace two As atoms on the row, which will create two undimerized As atoms with dangling bonds and indirectly pin the Fermi level. On the GaAs(001)-(2×4) surface, Ga_2O molecules preferentially bond to As dimer rows and form Ga-As bonds. At monolayer Ga₂O coverage, the GaAs(001)-(2×4) surface undergoes a surface reconstruction, resulting in (2×2) surface periodicity, which has completed As termination with Ga₂O molecules inserted in As dimer pairs on the row. This new surface and bonding restore near bulklike surface charges and unpin the surface after Ga₂O deposition. For the In₂O on the GaAs(001)- (2×4) surface, the As-As insertion site is not favorable for initial In₂O bonding. In₂O initially bonds in the trough regions forming stable In-O-In-Ga bonds. At higher coverage with postdeposition annealing, In₂O molecules start to insert in or between As dimers pairs on the row and bond with pre-existing first layer In₂O in the trough. STS spectra results show for both *p*-type and *n*-type samples, the Fermi level resides near the conduction band edge, which is consistent with the $In_2O/GaAs(001)-(2 \times 4)$ being pinned.

In₂O chemisorption on In_{0.53}Ga_{0.47}As(001)-(4×2) is completely different. In₂O molecules initially bond to As atoms at the edge of row and form In–O–In–As bonds. At high coverage with postdeposition annealing, In₂O molecules fill the trough region, bond together, and form relative long range ordered structure along the row in the [1 1 0] direction. These new In₂O–In/Ga trough bonding sites eliminate many of the strained unbuckled dimer atoms in the trough, which are responsible for the surface pinning. O atoms from In₂O molecules bond with In/Ga atoms in the trough to form new O–In/Ga bonding structure, which restores the trough group III atoms into a more bulklike tetrahedral sp³ bonding geometry and unpins the In_{0.53}Ga_{0.47}As(001)-(4×2) surface.

V. CONCLUSIONS

STM/STS is used to determine the atomic bonding geometry and electronic structures of In₂O adsorbed group IIIrich InAs(001)-(4×2) and In_{0.53}Ga_{0.47}As(001)-(4×2) surfaces. STM results show that without annealing, In atoms from In₂O bond with substrate As atoms at the edge of row to form In-O-In-As bonds. With postdeposition annealing, In₂O overcomes kinetic barriers and O atoms from In₂O bond with In/Ga atoms in the trough to form new In₂O-In/Ga bonds, which restores trough In/Ga atoms into a more bulklike tetrahedral sp³ bonding environment and releases the strain. This bonding is sufficiently favorable since In₂O-In/Ga trough sites are more stable than In-O-In-As edge sites by about $\sim 0.81 \text{ eV}/\text{In}_2\text{O}$ for InGaAs surfaces and ~ 0.77 eV/In₂O for InAs surfaces. High temperature postdeposition annealing results show an ordered In₂O monolayer with weak bonding since the layer can readily be desorbed without displacing surface atoms. STS spectra results clearly show In₂O deposited In_{0.53}Ga_{0.47}As(001)-(4 \times 2) surface has an unpinned interface after postdeposition annealing at 380 °C. This suggests that in the absence of a thermal oxidation or processing, which disrupts the surface, some oxides will be able to bond with InGaAs in a geometry, which eliminates the surface states within the bandgap. Although the process window is narrow, the result proves that oxide bonding can unpin a pinned III-V semiconductor surface, and the results provide a bonding model for this process.

ACKNOWLEDGMENTS

The authors would like to thank T. J. Grassman, T. Song, and J. B. Clemens for very helpful discussions, S. R. Bishop for one of the initial calculations, and T. Kaufman-Osborn for the manuscript proofreading. J. Shen gratefully acknowledges Ph.D. Foundation Fellowship from the Intel Corporation. This work was supported by Grant Nos. SRC-NCRC-1437.003 and FCRP-MSD-887.011, and NSF-DMR-0706243.

- ¹R. Chau, S. Datta, M. Doczy, B. Doyle, J. Kavalieros, and M. Metz, IEEE Electron Device Lett. **25**, 408 (2004).
- ² R. Chau, S. Datta, M. Doczy, B. Doyle, J. Jin, J. Kavalieros, A. Majumdar, M. Metz, and M. Radosavljevic, IEEE Trans. Nanotechnol. 4, 153 (2005).
- ³S. Datta, G. Dewey, J. M. Fastenau, M. K. Hudait, D. Loubychev, W. K. Liu, M. Radosavljevic, W. Rachmady, and R. Chau, IEEE Electron Device Lett. 28, 685 (2007).
- ⁴M. J. Hale, S. I. Yi, J. Z. Sexton, A. C. Kummel, and M. Passlack, J. Chem. Phys. **119**, 6719 (2003).
- ⁵A. Cappy, B. Carnez, R. Fauquembergues, G. Salmer, and E. Constant, IEEE Trans. Electron Devices **27**, 2158 (1980).
- ⁶See http://www.ioffe.ru/SVA/NSM/ for semiconductor materials' characteristics and properties.
- ⁷N. Li, E. S. Harmon, J. Hyland, D. B. Salzman, T. P. Ma, Y. Xuan, and P. D. Ye, Appl. Phys. Lett. **92**, 143507 (2008).
- ⁸ R. J. W. Hill, D. A. J. Moran, X. Li, H. Zhou, D. Macintyre, S. Thoms, A. Asenov, P. Zurcher, K. Rajagopalan, J. Abrokwah, R. Droopad, M. Passlack, and L. G. Thayne, IEEE Electron Device Lett. **28**, 1080 (2007).
- ⁹T. D. Lin, H. C. Chiu, P. Chang, L. T. Tung, C. P. Chen, M. Hong, J. Kwo, W. Tsai, and Y. C. Wang, Appl. Phys. Lett. **93**, 033516 (2008).
- ¹⁰ A. M. Sonnet, C. L. Hinkle, M. N. Jivani, R. A. Chapman, G. P. Pollack, R. M. Wallace, and E. M. Vogel, Appl. Phys. Lett. **93**, 122109 (2008).
- ¹¹Y. Xuan, Y. Q. Wu, and P. D. Ye, IEEE Electron Device Lett. **29**, 294 (2008).
- ¹²S. Ohkouchi and N. Ikoma, Jpn. J. Appl. Phys., Part 1 **33**, 3710 (1994).
- ¹³C. Kendrick, G. LeLay, and A. Kahn, Phys. Rev. B **54**, 17877 (1996).
 ¹⁴D. L. Feldwinn, J. B. Clemens, J. Shen, S. R. Bishop, T. J. Grassman, A.
- C. Kummel, R. Droopad, and M. Passlack, Surf. Sci. 603, 3321 (2009).
 ¹⁵ A. P. Kirk, M. Milojevic, J. Kim, and R. M. Wallace, Appl. Phys. Lett. 96, 202905 (2010).
- ¹⁶ P. A. Bone, J. M. Ripalda, G. R. Bell, and T. S. Jones, Surf. Sci. 600, 973 (2006).

- ¹⁷ J. Mirecki Millunchick, A. Riposan, B. J. Dall, C. Pearson, and B. G. Orr, Surf. Sci. 550, 1 (2004).
- ¹⁸C. L. Hinkle, M. Milojevic, E. M. Vogel, and R. M. Wallace, Appl. Phys. Lett. **95**, 151905 (2009).
- ¹⁹J. B. Clemens, E. A. Chagarov, M. Holland, R. Droopad, J. Shen, and A. C. Kummel, J. Chem. Phys. **133**, 154704 (2010).
- ²⁰ P. Kruse, J. G. McLean, and A. C. Kummel, J. Chem. Phys. **113**, 9217 (2000).
- ²¹ P. Kruse, J. G. McLean, and A. C. Kummel, J. Chem. Phys. **113**, 9224 (2000).
- ²²D. L. Winn, M. J. Hale, T. J. Grassman, J. Z. Sexton, and A. C. Kummel, J. Chem. Phys. **127**, 134705 (2007).
- ²³ S. I. Yi, P. Kruse, M. Hale, and A. C. Kummel, J. Chem. Phys. **114**, 3215 (2001).
- ²⁴ J. B. Clemens, S. R. Bishop, D. L. Feldwinn, R. Droopad, and A. C. Kummel, Surf. Sci. 603, 2230 (2009).
- ²⁵ J. Shen, J. B. Clemens, E. A. Chagarov, D. L. Feldwinn, W. Melitz, T. Song, S. R. Bishop, A. C. Kummel, and R. Droopad, Surf. Sci. 604, 1757 (2010).
- ²⁶ M. J. Hale, J. Z. Sexton, D. L. Winn, A. C. Kummel, M. Erbudak, and M. Passlack, J. Chem. Phys. **120**, 5745 (2004).
- ²⁷G. Kresse and J. Furthmuller, Phys. Rev. B **54**, 11169 (1996).
- ²⁸G. Kresse and J. Furthmuller, Comput. Mater. Sci. 6, 15 (1996).
- ²⁹ P. E. Blöchl, Phys. Rev. B **50**, 17953 (1994).
- ³⁰G. Kresse and D. Joubert, Phys. Rev. B **59**, 1758 (1999).
- ³¹J. P. Perdew, K. Burke, and M. Ernzerhof, Phys. Rev. Lett. 77, 3865 (1996).
- ³² J. P. Perdew, K. Burke, and M. Ernzerhof, Phys. Rev. Lett. 78, 1396 (1997).
- ³³J. E. Northrup and S. Froyen, Phys. Rev. Lett. **71**, 2276 (1993).
- ³⁴J. Neugebauer and M. Scheffler, Phys. Rev. B 46, 16067 (1992).
- ³⁵Q. Guo, M. E. Pemble, and E. M. Williams, Surf. Sci. **468**, 92 (2000).
- ³⁶J. Shen, W. Melitz, D. L. Feldwinn, S. Lee, R. Droopad, and A. C. Kummel, ECS Transactions 33, 105 (2010).
- ³⁷D. L. Winn, M. J. Hale, T. J. Grassman, A. C. Kummel, R. Droopad, and M. Passlack, J. Chem. Phys. **126**, 084703 (2007).
- ³⁸R. M. Feenstra, Phys. Rev. B **50**, 4561 (1994).
- ³⁹See supplementary material at http://dx.doi.org/10.1063/1.3497040 for energy eigenvalues and the occupations.
- ⁴⁰ J. Paier, M. Marsman, K. Hummer, G. Kresse, I. C. Gerber, and J. G. Angyan, J. Chem. Phys. **124**, 154709 (2006).
- ⁴¹ J. Heyd and G. E. Scuseria, J. Chem. Phys. **121**, 1187 (2004).
- ⁴²J. Heyd, G. E. Scuseria, and M. Ernzerhof, J. Chem. Phys. **118**, 8207 (2003).
- ⁴³ J. Heyd, G. E. Scuseria, and M. Ernzerhof, J. Chem. Phys. **124**, 219906 (2006).