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ATOMIC AND ELECTRONIC STRUCTURES OF OXIDES ON III-V SEMICONDUCTORS

A dissertation submitted in partial satisfaction of the requirements for the degree of

Doctor of Philosophy

in

Materials Science and Engineering

by

Jian Shen

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2010
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University of California, San Diego

2010
To my parents, wife and kids
# Table of Contents

Signature Page ........................................................................................................ iii

Dedication ................................................................................................................. iv

Table of Contents ..................................................................................................... v

List of Figures and Tables ....................................................................................... x

List of Abbreviations and Symbols ......................................................................... xiii

Acknowledgements ................................................................................................. xvi

Vita ............................................................................................................................ xix

Abstract of the Dissertation ................................................................................... xxii

Chapter 1 Introduction ............................................................................................. 1

1.1. Oxide/III-V Semiconductor Interface ................................................................. 1

1.2. Experimental and Computational Techniques .................................................... 2

1.2.1. Scanning Tunneling Microscopy .................................................................... 2

1.2.2. Scanning Tunneling Spectroscopy ................................................................. 5

1.2.3. Density Function of Theory .......................................................................... 6

1.3. Thesis Outline .................................................................................................... 6

References ................................................................................................................. 8

Chapter 2 Real Space Surface Reconstructions of Decapped As-rich
In$_{0.53}$Ga$_{0.47}$As(001)-(2×4) ...................................................................................... 10
# Chapter 3 Structural and Electronic Properties of Group III Rich In$_{0.53}$Ga$_{0.47}$As-(001)

<table>
<thead>
<tr>
<th>Section</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>3.1. Abstract</td>
<td>21</td>
</tr>
<tr>
<td>3.2. Introduction</td>
<td>22</td>
</tr>
<tr>
<td>3.3. Experimental and Theoretical Methods</td>
<td>24</td>
</tr>
<tr>
<td>3.4. Results and Discussion</td>
<td>26</td>
</tr>
<tr>
<td>3.4.1. Experimental Results</td>
<td>26</td>
</tr>
<tr>
<td>3.4.1.1. Room Temperature 300 K In$<em>{0.53}$Ga$</em>{0.47}$As Surface</td>
<td>26</td>
</tr>
<tr>
<td>3.4.1.2. Low Temperature 77 K In$<em>{0.53}$Ga$</em>{0.47}$As Surface</td>
<td>30</td>
</tr>
<tr>
<td>3.4.1.3. Electronic Properties of In$<em>{0.53}$Ga$</em>{0.47}$As Surface</td>
<td>34</td>
</tr>
<tr>
<td>3.4.2. Density Functions Theory Results</td>
<td>35</td>
</tr>
<tr>
<td>3.4.2.1. Trough structure</td>
<td>39</td>
</tr>
<tr>
<td>3.4.2.2. Row Structures</td>
<td>41</td>
</tr>
</tbody>
</table>
Chapter 6 Scanning Tunneling Microscopy/Spectroscopy Study of Atomic and Electronic Structures of In$_2$O on InAs and In$_{0.53}$Ga$_{0.47}$As(001)-(4×2)
6.5.3. Oxides on GaAs, InAs and InGaAs Comparison ....................................... 121

6.6. Conclusions ........................................................................................................ 122

6.7. Acknowledgements ............................................................................................. 123

References .................................................................................................................. 123
List of Figures and Tables

Figures

Figure 1.1. Schematic diagram of interface between high k oxide and III-V semiconductor...............................................................2

Figure 1.2. Schematic diagram of STM of the oxide deposited III-V semiconductor surface..........................................................3

Figure 1.3. Schematic diagram of tunneling process between semiconductor surface and metal tip....................................................4

Figure 2.1. Top-down view of atomic structure with the cross sections for In$_{0.53}$Ga$_{0.47}$As(001)-(4×3) and (2×4) surface reconstructions........................................13

Figure 2.2. Example of In$_{0.53}$Ga$_{0.47}$As(001)-(2×4) sample decapping and annealing procedure showing the chamber pressure (blue line), program temperature (black line)..........................................................14

Figure 2.3. Filled state STM images (25 × 25 nm$^2$) obtained from clean III-V surfaces. 16

Figure 2.4. STM images obtained from clean In$_{0.53}$Ga$_{0.47}$As(001) annealed at different temperatures..............................................................17

Figure 3.1. STM of In$_{0.53}$Ga$_{0.47}$As(001)-(4×2) at 300 K ..................................................28

Figure 3.2. STM of In$_{0.53}$Ga$_{0.47}$As(001)-(4×2) at 77 K. ...........................................30

Figure 3.3. The experimentally observed distribution of dimer lengths and spacings between dimers on InAs and InGaAs surfaces from 77 K LT-STM data. ..........................32

Figure 3.4. Scanning tunneling spectroscopy for the following group III rich In$_{0.53}$Ga$_{0.47}$As(001)-(4×2) surfaces..............................................................33

Figure 3.5. Summary of possible surface structures for InGaAs(001) according to DFT calculations. Only the top atomic layers are shown for clarity of presentation..................37

Figure 3.6. DFT molecular dynamics (MD) model of the row structures of InGaAs clean surface annealed at 900 K at different annealing times in femtoseconds (fs)........41
Figure 3.7. DFT relaxed atomic structures and density of states (DOS) curves for group III rich In$_{0.5}$Ga$_{0.5}$As(001) reconstructions ................................................................. 46

Figure 3.8. 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 ................................................................. 48

Figure 3.9. Row structures of InAs clean surface annealed at 900 K at different annealing times in femtosecond (fs). ................................................................. 53

Figure 3.10. LEED images of the group III-rich In$_{0.53}$Ga$_{0.47}$As(001)-(4×2) and InAs(001)-(4×2) surface at 300 K ................................................................. 56

Figure 4.1. Structure of clean InAs(001)-(4×2) at 300 K ................................................................. 64

Figure 4.2. Bonding of RT deposited In$_2$O/InAs(001)-(4×2) ................................................................. 65

Figure 4.3. Height analysis for RT deposition of In$_2$O/InAs(001)-(4×2) ................................................................. 67

Figure 4.4. Bonding of RT deposited In$_2$O/InAs(001)-(4×2) after a 380°C anneal ........ 69

Figure 4.5. Height analysis for RT deposition and 380°C annealing of In$_2$O/InAs(001)-(4×2) ................................................................. 70

Figure 4.6. STM image of the InAs(001)-(4×2) surface after low coverage SiO deposition (~ 4% ML) at 300 K with PDA ................................................................. 72

Figure 4.7. STM images and the height distributions of the InAs(001)-(4×2) surface after 35% coverage of SiO deposition. ................................................................. 74

Figure 4.8. The vapor pressure vs temperature for In$_2$O and SiO ................................................................. 76

Figure 5.1. A schematic diagram of the oxide deposition system ................................................................. 83

Figure 5.2. Filled state STM images taken at 300 K of the In$_{0.53}$Ga$_{0.47}$As(001) surface with schematic diagrams for three different reconstructions ................................................................. 85

Figure 5.3. Filled state STM images of Ga$_2$O deposited In$_{0.53}$Ga$_{0.47}$As(001)-(4×2) surface at 300 K ................................................................. 86

Figure 5.4. In$_2$O deposited In$_{0.53}$Ga$_{0.47}$As(001)-(4×2) surface. ................................................................. 90
Figure 5.5. Scanning tunneling spectra for the In$_{0.53}$Ga$_{0.47}$As(001)-(4×2) clean surface and Ga$_2$O deposited In$_{0.53}$Ga$_{0.47}$As(001)-(4×2) surface. ................................................................. 93

Figure 6.1. Dual state STM images of InAs(001)-(4×2) with atomic structure model. ........................................ 101

Figure 6.2. STM images and structure model with line scan of In$_2$O deposited on InAs(001)-(4×2) surface. .................................................................................................................. 103

Figure 6.3. STM images of medium coverage In$_2$O deposited on InAs(001)-(4×2) surface with two different post-deposition annealing................................................................. 104

Figure 6.4. STM images of high coverage In$_2$O deposited on InAs(001)-(4×2) surface with post-deposition annealing. .................................................................................. 107

Figure 6.5. A filled state ($V_s = -3$ V, $I_t = 0.15$ nA, 600 Å × 600 Å) STM image of the In$_{0.53}$Ga$_{0.47}$As(001)-(4×2) clean surface. ........................................................................ 108

Figure 6.6. STM images and structure model with of In$_2$O deposited on In$_{0.53}$Ga$_{0.47}$As(001)-(4×2) surface.. ........................................................................................................ 109

Figure 6.7. STM images of high coverage In$_2$O deposited on In$_{0.53}$Ga$_{0.47}$As(001)-(4×2) surface with post-deposition annealing......................................................... 111

Figure 6.8. Scanning tunneling spectra for the In$_{0.53}$Ga$_{0.47}$As(001)-(4×2) clean surface and monolayer coverage of In$_2$O. ............................................................................. 114

Figure 6.9. 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 (undimerized-buckled). ....................................... 117

Figure 6.10. DFT bonding structures of In$_2$O/In$_{0.5}$Ga$_{0.5}$As(001) and calculated density of states. ................................................................. 120

Table

Table 5.1. Annealing temperature regions for different surface reconstructions........... 84
**List of Abbreviations and Symbols**

<table>
<thead>
<tr>
<th>Abbreviation</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>AES</td>
<td>Auger electron spectroscopy</td>
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<tr>
<td>As</td>
<td>Arsenide</td>
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<tr>
<td>CBM</td>
<td>Conduction Band Minimum</td>
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<tr>
<td>CMOS</td>
<td>Complimentary Metal-Oxide Semiconductor</td>
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<tr>
<td>C-V</td>
<td>Capacitance-Voltage</td>
</tr>
<tr>
<td>DFT</td>
<td>Density Functional Theory</td>
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<tr>
<td>Dit</td>
<td>Interfacial Density of States</td>
</tr>
<tr>
<td>DOS</td>
<td>Density of States</td>
</tr>
<tr>
<td>$E_c$</td>
<td>Conduction Band Energy</td>
</tr>
<tr>
<td>$E_F$</td>
<td>Fermi Level Energy</td>
</tr>
<tr>
<td>$E_{\text{gap}}$</td>
<td>Energy difference between the conduction band and valence band</td>
</tr>
<tr>
<td>$E_v$</td>
<td>Valence Band Energy</td>
</tr>
<tr>
<td>eV</td>
<td>Electron Volt</td>
</tr>
<tr>
<td>FWHM</td>
<td>Full Width at Half Maximum</td>
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<tr>
<td>Acronym</td>
<td>Definition</td>
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<tr>
<td>---------</td>
<td>------------</td>
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<tr>
<td>Ga</td>
<td>Gallium</td>
</tr>
<tr>
<td>GGA</td>
<td>Generalized Gradient Approximation</td>
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<tr>
<td>In</td>
<td>Indium</td>
</tr>
<tr>
<td>$I_t$</td>
<td>Tunneling Current</td>
</tr>
<tr>
<td>LDOS</td>
<td>Local Density of States</td>
</tr>
<tr>
<td>LEED</td>
<td>Low Energy Electron Diffraction</td>
</tr>
<tr>
<td>MBE</td>
<td>Molecular Beam Epitaxy</td>
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<tr>
<td>MOSFET</td>
<td>Metal-Oxide Semiconductor Field-Effect Transistor</td>
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<tr>
<td>Oxygen</td>
<td>O</td>
</tr>
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<td>PAW</td>
<td>Projector Augmented-Wave</td>
</tr>
<tr>
<td>PBC</td>
<td>Periodic Boundary Conditions</td>
</tr>
<tr>
<td>PBE</td>
<td>Perdew-Burke-Ernzerhof</td>
</tr>
<tr>
<td>PDA</td>
<td>Post-Deposition Annealing</td>
</tr>
<tr>
<td>PP</td>
<td>Pseudo-Potentials</td>
</tr>
<tr>
<td>RHEED</td>
<td>Reflection High Energy Electron Diffraction</td>
</tr>
<tr>
<td>STM</td>
<td>Scanning Tunneling Microscopy</td>
</tr>
<tr>
<td>Abbreviation</td>
<td>Definition</td>
</tr>
<tr>
<td>--------------</td>
<td>----------------------------------</td>
</tr>
<tr>
<td>STS</td>
<td>Scanning Tunneling Spectroscopy</td>
</tr>
<tr>
<td>UHV</td>
<td>Ultra High Vacuum</td>
</tr>
<tr>
<td>VASP</td>
<td>Vienna Ab-Initio Simulation Package</td>
</tr>
<tr>
<td>VBM</td>
<td>Valence Band Maximum</td>
</tr>
<tr>
<td>$V_t$</td>
<td>Tunneling Voltage</td>
</tr>
<tr>
<td>XPS</td>
<td>X-ray Photoelectron Spectroscopy</td>
</tr>
</tbody>
</table>
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Chapter 3, in full, has been accepted for publication of the material as it appears in J. Shen, J. B. Clemens, E. A. Chagarov, D. L. Feldwinn, W. Melitz, T. Song, S.R. Bishop, R. Droopad, and A. C. Kummel, Structural and electronic properties of group III rich In_{0.53}Ga_{0.47}As(0 0 1), Surface Science (2010). The dissertation author was the primary investigator and author of this paper.

Chapter 4, in full, has been accepted for publication of the material as it appears in J. Shen, W. Melitz, D. L. Feldwinn, S. Lee, R. Droopad, and A. C. Kummel, Bonding Geometries at the In_2O and SiO/III-V Semiconductor Interface, ECS Transaction (2010). The dissertation author was the primary investigator and author of this paper.

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ABSTRACT OF THE DISSERTATION

ATOMIC AND ELECTRONIC STRUCTURES OF OXIDES ON III-V SEMICONDUCTORS

by

Jian Shen

Doctor of Philosophy in Materials Science and Engineering
University of California, San Diego, 2010
Professor Andrew C. Kummel, Chair

The surface reconstructions of decapped InAs(001) and In$_{0.53}$Ga$_{0.47}$As(001) have been studied using scanning tunneling microscopy (STM). Quantitative comparison of the In$_{0.53}$Ga$_{0.47}$As(001)-(4×2) and InAs(001)-(4×2) show the reconstructions are almost identical, but In$_{0.53}$Ga$_{0.47}$As(001)-(4×2) has at least a 4× higher surface defect density even on the best samples. For both In$_{0.53}$Ga$_{0.47}$As(001)-(4×2) and InAs(001)-(4×2), density functional theory (DFT) simulations at elevated temperature are consistent with the experimentally observed 300 K structure being a thermal superposition of three structures.

The passivation of InAs(001) and InGaAs(001) surface using three different oxides (SiO, Ga$_2$O and In$_2$O) was studied using STM, STS, and DFT modeling of bonding and electronic structures. SiO molecules have higher self-binding energy so that
they bond themselves and form nanoclusters on InAs(001)-(4×2) surface. Conversely, both Ga$_2$O and In$_2$O molecules bond to the As atoms at the edge of the rows. However, Ga$_2$O molecules also bond to preexisting Ga$_2$O oxide on the surface. At full coverage with post-deposition annealing, SiO oxide remains as nanoclusters, Ga$_2$O oxide forms disordered structures with the large flat terraces on the surface, while In$_2$O oxide bonds with the trough In atoms to form new O-In bonding sites and forms ordered structures running in the [110] direction on In$_{0.53}$Ga$_{0.47}$As(001)-(4×2). STS results show that Ga$_2$O oxide does not passivate the interface nor unpin the In$_{0.53}$Ga$_{0.47}$As(001)-(4×2) surface consistent with its inability to form monolayer ordered islands on the surface; conversely, In$_2$O/In$_{0.53}$Ga$_{0.47}$As(001)-(4×2) has an ordered monolayer coverage and is unpinned.
Chapter 1

Introduction

1.1. Oxide/III-V Semiconductor Interface

III-V compound semiconductors are promising channel materials for very high speed and low power logic applications. However, they are expensive and difficult to process. The main processing challenge for III-V semiconductors is that they do not have a native oxide which is insulating and has a low trap density; this is in contrast to silicon which has an excellent native oxide, SiO$_2$. The technological advance of SiO$_2$ as a gate oxide is the low interface trap density ($D_{it}$); for thermally grown SiO$_2$/Si after post-deposition hydrogen passivation, $D_{it}$ can be as low as $10^{10}$ cm$^{-2}$ eV$^{-1}$. Oxide-semiconductor interfaces are denoted as electrically passivated when the interface has a low enough trap density to allow the field from the gate oxide to bend the semiconductor bands thereby controlling the conductivity in the semiconductor channel. III-V materials have a high electron mobility, but it is extremely difficult to form an electrically passivated thermal oxide-semiconductor interface for III-V materials due to a large $D_{it}$, $10^{12}$ cm$^{-2}$ eV$^{-1}$, which will pin the Fermi level. Electrical pinning denotes the condition in which the interface trap density is so large that the electric field from the gate oxide cannot bend the semiconductor band and thereby cannot control the conductivity in the semiconductor channel. To develop practical III-V field effect transistors, it is important to determine and understand the interfacial bonding between the oxide and the III-V semiconductor, and the electronic structure of the interface so we can minimize the interface traps.
Fig. 1.1 shows a schematic diagram of the interface between the high k oxide and the III-V semiconductor. Both the semiconductor and oxide atoms at the interface are undercoordinated. These undercoordinated atoms have non-bonding orbitals which are denoted as “dangling bonds”. In general completely filled or completely empty dangling bonds do not have states in the semiconductor bandgap, but partially filled dangling bonds have states in the bandgap which can pin the Fermi level [1, 2]. For an oxide-semiconductor interface to be electrically passive, either there needs to be no interfacial dangling bonds or the dangling bonds cannot be partially filled.

Figure 1.1. Schematic diagram of the interface between the high k oxide and the III-V semiconductor [3].

1.2. Experimental and Computational Techniques

1.2.1. Scanning Tunneling Microscopy

The focus of this dissertation is to study the atomic and electronic structures of the oxide/semiconductor interface. The major technique used for characterizing surfaces and interfaces is scanning tunneling microscopy (STM), which records the surface morphology and electronic structure on an atomic level. In the three decades since
Binning and Rohrer invented STM in 1981 [4, 5], STM has been developed into a powerful tool with applications in many fields of science, ranging from condensed physics to biology [6].

Figure 1.2. Schematic diagram of an STM of the oxide deposited III-V semiconductor surface.

The basic mechanism of STM imaging is illustrated in Fig. 1.2; only three components are considered: tip, vacuum space, and sample. When the tip is brought very close to the sample (~ 10 Å) and a voltage is applied between the tip and sample, the electrons will tunnel through the vacuum barrier due to quantum mechanical effects. This tunneling current is given approximately by

$$I \propto V e^{-kz} \quad (1-1)$$

where $V$ is the applied voltage between the tip and the sample, $k$ is the decay length and $z$ is the tunneling gap between the tip and the sample surface. The exponential decay dependence between the tunneling current and the tunneling gap is the source of the high depth resolution of STM. In constant current mode imaging, as the tip scans across the
sample surface in the x and y directions as the current is measured, and, simultaneously, a feedback loop moves tip in the vertical direction (z) to maintain the constant tunneling current value. By recording the vertical movement of the scanning tip, the sample topography can be imaged and the atomic level surface structure can be studied. Normally, the measured equal-current contour lines are interpreted as real space surface topography. However, the STM image is actually a convolution of the electronic and topographic structure of sample surface since STM probes surface charge density. The other STM imaging mode is constant height where the tip height is held constant and current changes are imaged. In the studies described in this dissertation, only constant current mode was used.

![Diagram of tunneling process](image)

**Figure 1.3.** Schematic diagram of the tunneling process between the semiconductor surface and the metal tip. (a) Empty state and (b) filled state.
1.2.2. Scanning Tunneling Spectroscopy

The STM image is not just a topographical image of sample surface because the tunneling current strongly depends on the electronic density of states (DOS) of the surface. Scanning tunneling spectroscopy (STS) is employed to directly measure the DOS using the STM apparatus. Fig. 1.3 depicts the mechanism by which the filled states and empty states are probed by STM/STS techniques [6, 7]. When a negative bias is applied to the tip respective to the sample, the electrons will tunnel from tip states through vacuum barrier into empty states of the sample surface. When a positive bias is applied to the tip respective to the sample, the electrons will tunnel from filled states of sample surface through vacuum barrier into the tip. Therefore, information concerning the sample’s surface states can be obtained by ramping the applied voltage from negative to positive biases. According to Tersoff’s tunneling theory [8, 9], the differential conductance (dI/dV) spectra measurement can provide very useful information concerning the electronic structure of sample surface, for example, the local density of states (LDOS) of the surface at a particular energy.

There are two methods to acquire the dI/dV spectra. In the first method, the tip is moved to a spot above the sample surface with at fixed current I and voltage V. Afterwards, the tip’s position is fixed and the voltage V is ramped and an I-V curve is recorded. Based on the I-V data, the dI/dV can be calculated using a three point numerical derivative method

\[
\frac{\text{d}I}{\text{d}V} = \frac{I_{n+1}(V+\Delta V) - I_{n-1}(V-\Delta V)}{2\Delta V}.
\]

where \(\Delta V\) is the step of ramping voltage, \(I_{n-1}\) and \(I_{n+1}\) are measured currents at the \((n-1)\)th and the \((n+1)\)th steps, respectively. For the second method of acquiring dI/dV spectra, a
sinusoidal AC voltage is superimposed on the DC tip voltage V and the dI/dV signal is directly recorded by varying the tip voltage using a lock-in amplifier. Detailed knowledge of the STS technique can been found in Feenstra et al. and Tersoff et al.’s papers [8-13]. In the studies described in this dissertation, the second method was used.

1.2.3. Density Function Theory

Density functional theory (DFT) is an *ab-initio* quantum mechanical method used to investigate the electronic structure (principally the ground state) of many body systems. Using DFT, surface reconstructions, bonding structures and energies, and the electronic structures including band structures and density of states can be calculated.

In the studies described in this dissertation, STM was used to image both clean and oxide deposited III-V surfaces, which allows us to form empirical models of the surface structure and chemical bonding sites. However, even the best STM images cannot make definitive atomic bonding structure assignments for the surfaces. DFT can be used to calculate binding energies for different bonding sites to determine the most stable bonding geometry and confirm the empirical bonding sites assignments [14].

1.3. Outline of the Dissertation

This Ph.D. dissertation focuses on two III-V compound semiconductor InAs and In$_{0.53}$Ga$_{0.47}$As. In the first part of this dissertation, clean surface structures of InAs and In$_{0.53}$Ga$_{0.47}$As(001) including both (2×4) and (4×2) reconstructions were investigated using LEED and STM. The electronic structure of the In$_{0.53}$Ga$_{0.47}$As(001)-(4×2) surface was investigated using STS techniques. The second part of this dissertation focuses on
nanoscale characterization of oxide deposited InAs and InGaAs(001) interface, including SiO, Ga$_2$O and In$_2$O.

Chapter 2 reports upon an STM study of the surface reconstructions of decapped As-rich III-V compound semiconductors. It is shown that the As-rich α2(2×4) and β2(2×4) reconstructions, predicted by DFT for GaAs(001)-(2×4), InAs(001)-(2×4) and InGaAs(001)-(2×4) surfaces, were observed to coexist on In$_{0.53}$Ga$_{0.47}$As (001).

In chapter 3, room temperature (300 K) and low temperature (77 K) STM images of In/Ga rich In$_{0.53}$Ga$_{0.47}$As(001) are compared. DFT molecular dynamics (MD) simulations show that the 300 K structure is not a unique structure distinct from the 77 K structure. Instead, the experimentally observed 300 K structure is consistent with a thermal superposition of three structures including the 77 K structure. STS results show that there is a surface dipole or pinning states near the valence band (VB) for the 300 K In$_{0.53}$Ga$_{0.47}$As(001)-(4×2) surface which is consistent with DFT calculations. DFT calculations of the band-decomposed charge density indicate that the strained unbuckled trough dimers are responsible for the surface pinning. In the appendix, DFT-MD on the InAs(001)-(4×2) surface is presented and the same results are observed.

Chapter 4 presents an STM study of oxide monolayers and submonolayers formed by vapor deposition of In$_2$O and SiO on InAs(001)-(4×2). In$_2$O molecules initially bond with As atoms at the edge of the row. After post-deposition annealing, In$_2$O molecules bond with the trough In atoms to form new O-In bonding sites. In$_2$O oxide forms dense and flat monolayer island structures on the InAs(001)-c(8×2)/(4×2) surface. Conversely, SiO molecules have higher self-binding energy so they bond to themselves and form nanoclusters on the InAs(001)-c(8×2)/(4×2) surface.
Chapter 5 reports upon an STM investigation of the bonding geometries of two different oxides, Ga$_2$O and In$_2$O, on In$_{0.53}$Ga$_{0.47}$As(001)-(4×2). The results at low coverage show both Ga$_2$O and In$_2$O molecules bond to the As atoms at the edge of the rows. However, Ga$_2$O molecules also bond to preexisting Ga$_2$O oxide on the surface. At full coverage with post-deposition annealing, Ga$_2$O oxide forms disordered structures with the large flat terraces on the surface, while In$_2$O oxide forms ordered structures running in the [110] direction on In$_{0.53}$Ga$_{0.47}$As(001)-(4×2). STS results show that Ga$_2$O oxide does not passivate the interface nor unpin the In$_{0.53}$Ga$_{0.47}$As(001)-(4×2) surface which is consistent with its inability to form monolayer ordered islands on the surface.

Chapter 6 describes a study in which STM/STS is used to determine the atomic bonding geometry and electronic structures of In$_2$O adsorbed group III-rich InAs and In$_{0.53}$Ga$_{0.47}$As(001)-(4×2) surface. The results show that the In$_2$O forms an ordered monolayer on both InAs and InGaAs surfaces. High temperature post-deposition annealing results show an ordered In$_2$O monolayer with weak bonding since the layer can readily be desorbed without displacing surface atoms. STS spectra results clearly show the In$_2$O deposited In$_{0.53}$Ga$_{0.47}$As(001)-(4×2) surface has an unpinned interface after post-deposition annealing at 380 °C.

References


Chapter 2

Real Space Surface Reconstructions of Decapped As-rich

$\text{In}_{0.53}\text{Ga}_{0.47}\text{As}(001)-(2\times4)$

2.1. Abstract

The surface reconstructions of decapped $\text{In}_{0.53}\text{Ga}_{0.47}\text{As}(001)$ have been studied using scanning tunneling microscopy (STM). It is shown that the As-rich $\alpha(2\times4)$ and $\beta(2\times4)$ reconstructions, predicted by density function theory (DFT) [1-3] for GaAs(001)-(2×4), InAs(001)-(2×4) and InGaAs(001)-(2×4) surfaces, were observed to coexist on $\text{In}_{0.53}\text{Ga}_{0.47}\text{As}(001)$. In contrast to molecular beam epitaxy (MBE) grown $\text{In}_{0.53}\text{Ga}_{0.47}\text{As}(001)$, the STM results on decapped $\text{In}_{0.53}\text{Ga}_{0.47}\text{As}(001)$ do not show the existence of the heterodimer $\text{In}_{0.53}\text{Ga}_{0.47}\text{As}(001)-(4\times3)$ structure [4-5]. At the intermediate annealing temperature ranges of 400 - 440°C, a $(2\times4)-(4\times2)$ mixed surface reconstruction was observed. When $\text{In}_{0.53}\text{Ga}_{0.47}\text{As}(001)/\text{InP}$ sample was annealed between 440°C and 470°C, a pure In/Ga–rich $(4\times2)$ surface reconstruction was observed.
2.2. Introduction

The integrated circuit (IC) industry has been geometrically scaling the physical dimension of complementary metal-oxide semiconductor (CMOS) devices. Silicon based metal oxide semiconductor field effect transistor (MOSFET) technology may be approaching its theoretical physical limits [6-7]. Therefore, the IC industry may need alternative materials to continue progress in device scaling. A group of materials that might provide a solution are III-V compound semiconductors because they exhibit ~5-20 times higher effective channel mobility, enabling much lower supply voltage (~0.5 V) than silicon [6-7]. The key to fabricating a practical III-V MOSFET is forming an unpinned oxide-semiconductor interface with low fixed charge and low trap density [8]. A high quality interface of oxide and III-V compound semiconductor has been found to be related to the semiconductor surface reconstruction [8-9].

In$_{0.53}$Ga$_{0.47}$As is a convenient III-V compound semiconductor for a MOSFET channel material due to its high electronic mobility (~14,000 cm$^2$ V$^{-1}$ s$^{-1}$), high breakdown field, and its ability to be grown lattice matched to a semi-insulator substrate, InP. Although GaAs(001) [2, 11] and InAs(001) [12-14] have been the focus of many scanning tunneling microscopy (STM) studies, very few STM studies of have been performed on In$_{0.53}$Ga$_{0.47}$As(001) to understand and characterize the real space atomic surface structure [4-5]. Millunchick et al. performed STM studies of three different In composition InGaAs(001) films, grown at a single temperature by molecular beam epitaxy (MBE) to identify the different As-rich surface reconstructions that were present on InGaAs(001). They found that the surface of In$_{0.53}$Ga$_{0.47}$As/InP(001) films has a heterodimer (4×3) [Fig. 2.1(a)] surface reconstruction, the surface of
In$_{0.27}$Ga$_{0.73}$As/GaAs(001) films has a mixed heterodimer (4×3) and As-dimer α$_2$(2×4) [Fig. 2.1(b)] surface reconstruction, and the surface of In$_{0.81}$Ga$_{0.19}$As/InP(001) films has a mixed heterodimer (4×3) and As-dimer β$_2$(2×4) [Fig. 2.1(c)] surface reconstruction [4].

The (4×3) surface reconstruction is dramatically different from the two (2×4) [α$_2$(2×4) and β$_2$(2×4)] reconstructions, which have similarities to each other. The (4×3) surface reconstruction has the unit cell which contains three Ga/In dimers and one heterodimer in the top layer along with one As dimer in the third layer [Fig. 2.1(a)]. Conversely, the (2×4) surface reconstructions, both have a top row of dimerized As atoms which are bonded to tricoordinated In/Ga atoms. Between the As rows are trough regions that contains one As dimer per unit cell. The main difference between the α$_2$(2×4) and β$_2$(2×4) structures is that α$_2$ structure has single As dimer on the row [Fig 2.1(b)] and the β$_2$ structure has double As dimers on the row [Fig 2.1(c)]. In addition, the α$_2$ reconstruction has two degenerate reconstructions; the As dimer can either be on the left or the right of the row. This degeneracy causes the surface structure appears to have rows that are not completely straight in STM images.

In the present paper, the surface reconstructions of As-rich In$_{0.53}$Ga$_{0.47}$As(001)-(2×4) were further explored by STM using a decapping and annealing procedure over a range of temperatures. STM images of the In$_{0.53}$Ga$_{0.47}$As(001)-(2×4) showed that the surface contained the mixed single As-dimer α$_2$(2×4) [Fig. 2.1(b)] and double As-dimer β$_2$(2×4) [Fig. 2.1(c)] reconstruction, which density function theory (DFT) calculations [1-3] predict are stable for GaAs(001)-(2×4), InAs(001)-(2×4) and InGaAs(001)-(2×4) surfaces. As the annealing temperature was increased, the surface reconstruction of decapped In$_{0.53}$Ga$_{0.47}$As(001) changes to a (2×4)-(4×2) mixed reconstructions. For higher
annealing temperatures, the surface reconstruction of decapped In$_{0.53}$Ga$_{0.47}$As(001) changes to the In/Ga-dimer (4×2) without a heterodimer (4×3) surface reconstruction.

![Diagram of atomic structures with cross sections for In$_{0.53}$Ga$_{0.47}$As(001)-(4×3) and (2×4) surface reconstructions.](image)

**Figure 2.1.** Top-down view of atomic structure with the cross sections for In$_{0.53}$Ga$_{0.47}$As(001)-(4×3) and (2×4) surface reconstructions. (a) (4×3) [4], (b) α2(2×4) and (c) β2(2×4).

### 2.3. Experimental Method

MBE was employed to grow 0.2 μm of $1\times10^{18}$ cm$^{-3}$ doped In$_{0.53}$Ga$_{0.47}$As layer, lattice-matched to 500 μm thick InP(001) substrates with $1\times10^{18}$ cm$^{-3}$ doping. Experiments were performed on both $n$-type and $p$-type wafers. The re-grown wafers were capped in situ with a 50 nm protective arsenic cap. The wafers were transferred to a vacuum container for transporting to the STM chamber. The STM chamber is equipped with low energy electron diffraction (LEED) for confirmation of the surface periodicity and an Omicron VT STM.
Figure 2.2. Example of In$_{0.53}$Ga$_{0.47}$As(001)-(2×4) sample decapping and annealing procedure showing the chamber pressure (blue line), program temperature (black line). Peaks A, B and C in the pressure plot correspond to pressure bursts due to degassing, arsenic decapping and high temperature annealing, respectively.

The As capped samples were radiatively heated to obtain the desired In$_{0.53}$Ga$_{0.47}$As(001) surface reconstruction. Figure 2.2 shows the temperature ramps and subsequent pressure rise during the preparation of In$_{0.53}$Ga$_{0.47}$As(001)-(2×4). A three step decapping and annealing procedure was performed. First, the samples were initially held at 180°C for at least 2 hours degassing. This removed the weakly bonded impurities from the surface such as water. Second, the sample temperature was raised to 330°C for typically between 2 and 4 hours. This removed the As-cap. Finally, the sample was gradually heated to the peak temperature following by quenching. The peak temperature determined the observed surface reconstruction. For example, In$_{0.53}$Ga$_{0.47}$As(001)-(2×4), mixed (2×4) and (4×2), and pure (4×2) surfaces were observed at 380°C, 400-440°C and 455°C peak temperatures.
Following the As-decapping and annealing procedure, the surface reconstruction was verified by LEED. Afterwards, the sample was transferred to the STM. STM images were taken at room temperature using constant-current mode with a tunneling current of 100 pA and sample bias voltage of -2 V relative to the etched tungsten tip.

2.4. Results and Discussion

The $\alpha_2(2\times4)$ and $\beta_2(2\times4)$ are the most common reconstructions for III-V (2×4) surfaces. DFT calculations showed $\alpha_2$ and $\beta_2$ structures are the stable reconstructions for GaAs(001)-(2×4) [1-2], InAs(001)-(2×4) [1] and In$_{0.53}$Ga$_{0.47}$As(001)-(2×4) [3] surfaces. The atomic models of $\alpha_2(2\times4)$ and $\beta_2(2\times4)$ along with the Millunchick (4×3) model are schematically shown in Fig. 2.1. Figure 2.3(a) shows a filled state STM image of the clean In$_{0.53}$Ga$_{0.47}$As(001)-(2×4) surface. To deduce the In$_{0.53}$Ga$_{0.47}$As(001)-(2×4) surface reconstruction, the STM image was compared to filled state STM images of the GaAs(001)-(2×4) [Fig. 2.3(b)] and InAs(001)-(2×4) surfaces [Fig. 2.3(c)]. The STM images show that the In$_{0.53}$Ga$_{0.47}$As(001)-(2×4) more closely resembles the InAs(001)-(2×4) than the GaAs(001)-(2×4). However, small regions of the In$_{0.53}$Ga$_{0.47}$As(001)-(2×4) image are similar to the GaAs(001)-(2×4) image.
The GaAs(001)-(2×4) [Fig. 2.3(b)] surface has a nearly perfect β2(2×4) reconstruction with the exception of a few missing arsenic dimers that are caused by thermal desorption; this surface has been studied by many research groups [8, 15-16]. The α2(2×4) surface reconstruction has never been observed on GaAs(001). However, DFT calculations predict that it is also a stable surface reconstruction for GaAs(001) [1]. In comparison, the InAs(001)-(2×4) [Fig. 2.3(c)] surface is dominated by the α2(2×4) reconstruction with its zig-zagging rows. Although the current InAs(001)-(2×4) surface is made up almost entirely of α2(2×4), if the annealing temperature is decreased, an increasing amount of β2(2×4) areas will be observed on the surface. The β2(2×4) reconstruction which has a double top As dimers row was observed by Ratsch et al. under As rich conditions on InAs(001) grown by in situ MBE [1]. The In$_{0.53}$Ga$_{0.47}$As(001)-(2×4) [Fig. 2.3(a)] surface exhibits zig-zagging rows which is indicative of α2(2×4) reconstruction. However, there is a 2 to 4 times higher faction of double As-dimers on the row of In$_{0.53}$Ga$_{0.47}$As(001)-(2×4) surface than on the row of InAs(001)-(2×4) based on the current STM images.
Figure 2.4. STM images obtained from clean In$_{0.53}$Ga$_{0.47}$As(001) annealed at (a) 380°C As-rich (2×4), (b) 437°C mixed (2×4)-(4×2), and (c) 455°C group III-rich (4×2).

The surface reconstructions were investigated on In$_{0.53}$Ga$_{0.47}$As(001)/InP as a function of the substrate temperature. There are three temperature regimes: (i) low temperature 330-400°C, (ii) intermediate temperature 400-440°C and (iii) high temperature 440-470°C. (i) When the sample was annealed between 330°C (As decapping temperature) and 400°C, the As-dimer (2×4) reconstruction was observed. As shown in Fig. 2.4(a), the As rich- In$_{0.53}$Ga$_{0.47}$As(001)-(2×4) surface structure is primarily made up of α2(2×4) with small regions of β2(2×4). The optimal temperature for preparing In$_{0.53}$Ga$_{0.47}$As(001)-(2×4) is 380°C. (ii) When the sample annealing temperature was between 400-440°C, a mixed as-dimer (2×4)/(4×2) reconstruction was observed without any regions of the heterodimer (4×3). It is possible that the heterodimer (4×3) regions can only be generated by in situ MBE which allows control of As flux as well as surface temperature. As shown in Fig 2.4(b), the (2×4) terraces are a monolayer step above the (4×2) terraces. The same mixed surface reconstruction has been previously reported for InAs(001) surface [17], but this mixed (2×4)/(4×2) surface structure has never been observed in GaAs(001). (iii) When the sample was annealed between 440°C and 470°C, the In/Ga dimer In$_{0.53}$Ga$_{0.47}$As(001)-(4×2) surface reconstruction was observed. As shown in Figure 2.4(c) the (4×2) surface has an In/Ga dimer (4×2)
reconstruction across the entire surface. The clean In\textsubscript{0.53}Ga\textsubscript{0.47}As(001)-(4×2) surface was found to closely resemble the InAs(001)-(4×2) surface and was dissimilar to well documented the GaAs(001)-\(\zeta(4\times2)\) surface [2]. Details of the GaAs(001)-(4×2), InAs(001)-(4×2) and In\textsubscript{0.53}Ga\textsubscript{0.47}As(001)-(4×2) have been discussed elsewhere [18-19]. Heating above 470°C induces surface disorder probably from depletion of As from the bulk.

2.5. Conclusions

In conclusion, high resolution STM images of the decapped In\textsubscript{0.53}Ga\textsubscript{0.47}As(001)-(2×4) surface reconstruction have been obtained. The (2×4) surface reconstruction is dominated by \(\alpha2(2\times4)\) structure, which contains zig-zagging row features in the STM images. However, there is a 2 to 4× higher fraction of double As dimers on the rows of the In\textsubscript{0.53}Ga\textsubscript{0.47}As(001)-(2×4) surface than on the rows of the InAs(001)-(2×4) surface. The surface reconstruction of decapped In\textsubscript{0.53}Ga\textsubscript{0.47}As(001)/InP changes with increasing annealing temperature first to a mixed (2×4)-(4×2) surface reconstruction between 400 - 440°C and finally to a pure In/Ga dimer (4×2) structure for temperatures in excess of 440°C.

2.6. Acknowledgments

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Chapter 2, in full, is a reprint of the material as it appears in J. Shen, D. L. Winn, W. Melitz, J. B. Clemens and A.C. Kummel, *Real Space Surface Reconstructions of Decapped As-rich In$_{0.53}$Ga$_{0.47}$As(001)-(2x4)*, ECS Transaction, 16(5) 463-468 (2008).

The dissertation author was the primary investigator and author of this paper.

**References**


Chapter 3

Structural and Electronic Properties of Group III Rich

In$_{0.53}$Ga$_{0.47}$As(001)

3.1. Abstract

The structural and electronic properties of group III rich In$_{0.53}$Ga$_{0.47}$As(001) have been studied using scanning tunneling microscopy/spectroscopy (STM/STS). At room temperature (300 K), STM images show that the In$_{0.53}$Ga$_{0.47}$As(001)-(4×2) reconstruction is comprised of undimerized In/Ga atoms in the top layer. Quantitative comparison of the In$_{0.53}$Ga$_{0.47}$As(001)-(4×2) and InAs(001)-(4×2) show the reconstructions are almost identical, but In$_{0.53}$Ga$_{0.47}$As(001)-(4×2) has at least a 4× higher surface defect density even on the best samples. At low temperature (77 K), STM images show that the most probable In$_{0.53}$Ga$_{0.47}$As(001) reconstruction is comprised of one In/Ga dimer and two undimerized In/Ga atoms in the top layer in a double (4×2) unit cell. Density functional theory (DFT) simulations at elevated temperature are consistent with the experimentally observed 300 K structure being a thermal superposition of three structures. DFT molecular dynamics (MD) show the row dimer formation and breaking is facilitated by the very large motions of tricoordinated row edge As atoms and z motion of In/Ga row atoms induced changes in As-In/Ga-As bond angles at elevated temperature. STS results show there is a surface dipole or the pinning states near the valence band (VB) for 300 K In$_{0.53}$Ga$_{0.47}$As(001)-(4×2) surface consistent with DFT calculations. DFT calculations of the band-decomposed charge density indicate that the strained unbuckled trough dimers being responsible for the surface pinning.
3.2. Introduction

III-V compound semiconductors are becoming increasingly important for a wide range of potential applications such as optoelectronic devices and high-speed, low-power logic applications, owing to their high electron mobilities, direct bandgaps, and high breakdown voltages. Nearly all these devices employ oxide-semiconductor, metal-semiconductor, or semiconductor-semiconductor interfaces. Therefore, it is necessary to understand the chemistry and physics of III-V compound semiconductors’ atomic-scale surface reconstructions since they play a critical role in interface formation.

In$_{0.53}$Ga$_{0.47}$As is a convenient III-V compound semiconductor for a metal–oxide–semiconductor field-effect transistor (MOSFET) channel material due to its high electronic mobility (~14,000 cm$^2$ V$^{-1}$ s$^{-1}$), high breakdown field, and its ability to be grown lattice matched on the semi-insulator substrate, InP. The key to fabricating a practical III-V MOSFET is forming an unpinned oxide-semiconductor interface with low fixed charge and low trap density. The interface quality between the oxide and III-V compound semiconductor has been found to correlate with the type of semiconductor surface reconstruction [1]. Although the As-rich InGaAs(001)-(2×4) and (4×3) reconstructions have been the focus of many scanning tunneling microscopy (STM) investigations and a few theoretical studies [2-4], there is still no consensus on the surface structure of the group III rich In$_{0.53}$Ga$_{0.47}$As(001)-(4×2). The group III rich reconstructions may be especially important for gate oxides deposition. It is likely that the As-rich (2×4) reconstruction undergoes oxygen induced displacement reactions during gate oxide deposition because the dimerized arsenic atoms are likely to be displaced by ambient oxygen during oxide deposition [5-8]. Conversely, the group III
rich (4×2) reconstructions are less reactive to oxygen and, therefore, probably more suitable for oxide deposition [9].

In this report, the first study of the surface reconstructions of the group III rich \( \text{In}_{0.53} \text{Ga}_{0.47} \text{As}(001) \) at both 300 K room temperature (RT) and 77 K low temperature (LT), using STM is presented. STM images of the \( \text{In}_{0.53} \text{Ga}_{0.47} \text{As}(001) \) show that the surface structures are different at 300 K and 77 K. At 300 K, the \( \text{In}_{0.53} \text{Ga}_{0.47} \text{As}(001)-(4\times2) \) surface appears to have only undimerized group III In/Ga topmost row atoms. At 77 K, the \( \text{In}_{0.53} \text{Ga}_{0.47} \text{As}(001)-(4\times2) \) surface has both undimerized and dimerized group III In/Ga topmost row atoms. The RT and LT reconstructions observed by STM for \( \text{In}_{0.53} \text{Ga}_{0.47} \text{As}(001)-(4\times2) \) are nearly identical to those observed by STM for \( \text{InAs}(001)-(4\times2) \). Standard DFT shows a bandgap for \( \text{InGaAs}(001) \) in contrast to \( \text{InAs}(001) \); therefore, the modeling of \( \text{InGaAs}(001) \) allows reasonably accurate calculations of the electronic structure for comparison to experimental results. For both \( \text{In}_{0.53} \text{Ga}_{0.47} \text{As}(001)-(4\times2) \) and \( \text{InAs}(001)-(4\times2) \) density functional theory (DFT) simulations predict that undimerized and dimerized structures have an energy difference of less than 10 meV per surface atom consistent with the 300 K structure not being a completely different structure than the 77 K structure but instead being a thermal superposition of three nearly degenerate structures; this was confirmed using DFT molecular dynamics (MD) simulations at elevated temperature. Both scanning tunneling spectroscopy (STS) and DFT calculations show that the \( \text{In}_{0.53} \text{Ga}_{0.47} \text{As}(001)-(4\times2) \) 300 K structure is pinned.
3.3. Experimental and Theoretical Methods

MBE was employed to grow a 0.2 μm layer of $1 \times 10^{18}$ cm$^{-3}$ doped In$_{0.53}$Ga$_{0.47}$As, lattice matched on 500 μm thick InP(001) substrates (Wafer Technology) with $1 \times 10^{18}$ cm$^{-3}$ doping. Experiments were performed on both $n$-type and $p$-type wafers. The regrown wafers were capped in situ with a 50 nm protective As$_2$ cap. The wafers were transferred to a vacuum container for transporting to the STM chamber. The STM chamber is equipped with low energy electron diffraction (LEED) for determination of the surface periodicity. Omicron VT-STM and LT-STM spectrometers were employed for determination of atomic structure at 300 K and 77 K. All the experiments were performed in ultra-high vacuum (UHV) systems with a background pressure less than $8 \times 10^{-11}$ Torr. The As$_2$ capped samples were radiatively heated to obtain the desired In$_{0.53}$Ga$_{0.47}$As(001) surface reconstruction. A three step decapping and annealing procedure was performed. First, the samples were initially held at 180 °C for at least 2 hours of degassing. This removed the weakly bonded impurities from the surface such as water. Second, the sample temperature was raised to 330 °C for typically between 2 and 4 hours to remove the As-cap. Finally, the sample was gradually heated to the peak temperature (around 450 °C for InAs(001)-(4×2) and 460 °C for In$_{0.53}$Ga$_{0.47}$As(001)-(4×2) ) and held for 15 minutes followed by a quick quenching. Following the As-decapping and annealing procedure, the surface reconstruction was verified by LEED. Afterwards, the sample was transferred into the STM chamber. STM images were taken at both 300 K room temperature and 77 K low temperature. Typical imaging conditions for both room temperature and low temperature are constant-current mode with a typical
50-100 pA setpoint tunneling current and -2 V sample bias voltage relative to the tungsten tip.

All DFT simulations were performed with the Vienna Ab-initio Simulation Package (VASP) [10,11] using projector augmented-wave (PAW) pseudo-potentials (PP) [12,13] and PBE (Perdew-Burke-Ernzerhof) exchange-correlation functional [14,15]. The choice of PBE functional and PAW PP’s was validated by parametrization runs demonstrating good reproducibility of experimental lattice constants, bulk moduli, and formation energies for bulk crystalline GaAs, and InAs. A Brillouin zone integration was performed at 4×4×1 Monkhorst-Pack k-point mesh with 9 irreducible k-points and a plane wave energy cut-off of 250 eV. A double (4×2) reconstructed unit cell (~16.95 × 16.95 Å², 140 atoms) was used, consisting of 7 atomic layers with a (001) surface orientation. The bottom layer As atoms were passivated by H atoms with fractional 3/4 |e| charge to mimic a continuous InGaAs bulk according to Ref. [16]. The slabs were relaxed using Conjugate-Gradient (CG) relaxation algorithms with 0.05 eV/Å force tolerance level. During relaxation, the three bottom layers were fixed in their bulk positions. A vacuum layer of ~12 Å was added over the slabs to eliminate spurious interaction through periodic boundary conditions (PBC). To compensate for spurious electric field induced by PBC for this type of system, a dipole correction was applied [10,11,17]. The preliminary In₀.₅Ga₀.₅As bulk unit cell was formed from GaAs unit cell by substituting half of Ga atoms by In atoms following checkerboard pattern and DFT optimizing the lattice constant of the alloy to equilibrium value. All slab total energies are reported per double (4×2) unit cell.
3.4. Results and Discussion

3.4.1. Experimental Results

3.4.1.1. Room Temperature 300 K In$_{0.53}$Ga$_{0.47}$As Surface

Shown in Fig. 3.1(a) is a typical large scale filled state RT-STM image of In$_{0.53}$Ga$_{0.47}$As(001) surface after As-decapping and annealing at 460 °C. The surface exhibits large, well-ordered, flat terraces. The main feature for the group III rich In$_{0.53}$Ga$_{0.47}$As(001) surface is rows running in the [110] direction. The distance between the rows is 17 Å. Between the rows are trough regions. STM images reveal that this (4×2) surface is similar to the surface reconstructions of several other low bandgap III-V materials like InSb(001)-(4×2) and InAs(001)-(4×2) surfaces, which have been observed by several groups [18-23]. However it is distinct from the Ga-rich GaAs(001)-(4×2) reconstruction [24-29]. Detailed reports of the surface reconstructions on GaAs(001) can been found in reports by Northrup et al. and Chadi et al. [24,30-33].

A quantitative comparison of the surface defect density on InAs(001)-(4×2) and In$_{0.53}$Ga$_{0.47}$As(001)-(4×2) was performed. Filled state STM images of group III rich InAs(001)-(4×2) and In$_{0.53}$Ga$_{0.47}$As(001)-(4×2) surface are shown in Figs. 3.1(a) and 3.1(b) for comparison. The absence of chemical impurities on the surface was confirmed by X-ray photoelectron spectroscopy (XPS): no C and O peaks were found on the clean surface. For both clean (4×2) surfaces, there are at least four kinds of defects on the both surfaces. Fig. 3.1(a) show the following defects types (Dn): D$_1$ as dark cuts on the row, D$_2$ as protrusion dots between the rows, D$_3$ domain boundaries as depression lines in the [-110] direction and D$_4$ domain boundaries as protrusion lines in the [110] direction. It is difficult to compare D$_2$, D$_3$ and D$_4$ defects between InAs and In$_{0.53}$Ga$_{0.47}$As clean surfaces
because quantities of these three defects are small or almost zero on the InAs(001)-(4×2) clean surface, so statistical errors are likely to occur. Therefore, only D₁ defects are analyzed. For the D₁ defects in Fig. 3.1(a), there are 108 defects on the rows in 75 nm × 75 nm In₀.₅₃Ga₀.₄₇As(001)-(4×2) surface. For the same size InAs(001)-(4×2) surface, there are only 23 D₁ defects on the rows. Therefore, there are at least 4 times more D₁ defects on the In₀.₅₃Ga₀.₄₇As(001)-(4×2) clean surface than on the InAs(001)-(4×2) clean surface since Fig. 3.1(a) represents one of the best In₀.₅₃Ga₀.₄₇As(001)-(4×2) surface that has been prepared while the InAs(001)-(4×2) in Fig. 3.1(b) is a typical surface.
Figure 3.1. STM of In$_{0.53}$Ga$_{0.47}$As(001)-(4×2) at 300K. (a) Filled state (sample voltage -2 V, 75 nm x 75 nm) RT-STM image of the group III rich In$_{0.53}$Ga$_{0.47}$As(001)-(4×2) surface. (b) Filled state (sample voltage -2 V, 75 nm x 75 nm) RT-STM image of the group III rich InAs(001)-(4×2) surface. (c) Filled state (sample voltage -2.5 V, 38 nm x 20 nm) RT-STM image of the group III rich In$_{0.53}$Ga$_{0.47}$As(001)-(4×2) surface with higher trough resolution where the bright balls completely fill in the trough region. (d) Same conditions as Fig. 3.1(c) except that the bright balls only partially fill in the trough region. (e) Ball-and-stick diagram of the group III rich In$_{0.53}$Ga$_{0.47}$As(001)-(4×2) at RT.

There are at least four kinds of defects on the surface: D$_1$ as dark cuts on the row, D$_2$ as protrusion dots between the rows, D$_3$ domain boundaries as depression lines in the [-110] direction, and D$_4$ domain boundaries as protrusion lines in the [110] direction.
Based on STM results, a RT \text{In}_{0.53}\text{Ga}_{0.47}\text{As}(001)-(4\times2) structure model is proposed in Fig. 3.1(e) that shows undimerized In/Ga atoms in the top layer. The small scale filled state RT-STM images of the \text{In}_{0.53}\text{Ga}_{0.47}\text{As}(001)-(4\times2) surface in Figs. 3.1(c) and 3.1(d) show more detailed information about the trough regions. For the RT \text{In}_{0.53}\text{Ga}_{0.47}\text{As}(001), bright balls are imaged in the trough regions. The distance between the bright balls in the trough regions is 8.5 Å which is close to 2× the span of the \text{In}_{0.53}\text{Ga}_{0.47}\text{As}(001) bulk unit cell (4.15 Å). However, the bright balls are not observed on \text{InSb}(001)-(4\times2) and \text{InAs}(001)-(4\times2) trough regions[18-23]. Conversely, the bright balls in the trough are observed for InAs growth on GaAs(001) surface by Xu et al. [34] and for indium-adsorbed onto the GaP(001) surface by Shimomura et al. [35], but the bright balls in the present study of group III rich \text{In}_{0.53}\text{Ga}_{0.47}\text{As}/\text{InP}(001) are smaller. In the present study of \text{In}_{0.53}\text{Ga}_{0.47}\text{As}/\text{InP}(001)-(4\times2), the bright balls sometimes completely fill in the trough regions as shown in Fig. 3.1(c), and sometimes only partially fill in the trough regions as shown in Fig. 3.1(d). It is possible that these bright balls result from excess charges rather than atomic clusters, similar to what has been observed on the clean GaAs(001)-(4×2) surface [36,37]. However, further experiments are needed to better understand these results. Due to the lack of a regular, ordered existence of the bright balls on the surface and the fact that the bright balls appear to result from electrostatic rather than geometric origins, they will therefore not be considered for structural assignment on the \text{In}_{0.53}\text{Ga}_{0.47}\text{As}(001)-(4\times2) surface.
Figure 3.2. STM of In$_{0.53}$Ga$_{0.47}$As(001)-(4×2) at 77K. (a) A filled state (sample voltage -2 V, 30 nm × 30 nm) LT-STM image of the group III rich In$_{0.53}$Ga$_{0.47}$As(001) surface. (b) Expanded LT-STM image taken from the green box in Fig. 3.2(a). (c) Ball-and-stick diagram of the group III rich In$_{0.53}$Ga$_{0.47}$As(001) at LT. Note that the 8 black dots in Fig. 3.2(b) correspond to 8 In/Ga atoms on two In/Ga rows in Fig. 3.2(c), 4 of them are dimerized and 4 of them are undimerized.

3.4.1.2. Low Temperature 77 K In$_{0.53}$Ga$_{0.47}$As Surface

Fig. 3.2(a) shows a filled state STM image of group III rich In$_{0.53}$Ga$_{0.47}$As(001) at low temperature (77 K). The LT-STM image pattern is distinctly different than the RT-STM image pattern, especially in rows along [110] direction [Figs. 3.2(a) and 3.2(b)]. At 77 K, the space between the vertical rows is still 17 Å (4×) in the [-110] direction. However, the rows at LT are not continuous; instead, they are composed of separated bright blocks predominantly spaced 17 Å apart (4×) in the [110] direction. In the trough regions between the rows, no structure could be resolved. Based on STM images, a LT In$_{0.53}$Ga$_{0.47}$As(001) structure model is proposed. Fig. 3.2(c) shows the ball-and-stick diagram of In$_{0.53}$Ga$_{0.47}$As at LT. This structure consists of one In/Ga dimer and two undimerized In/Ga atoms per double (4×2) unit cell in the top layer [20]; note the detailed DFT results are explained in the calculations section. The positions of In/Ga dimer and
undimerized In/Ga atoms in the row are assigned as black balls shown in Fig. 3.2(b). The distribution analysis of dimer and spacing between dimers has been performed on InAs and InGaAs surfaces based on 77 K LT-STM data to determine most probable surface structures. The analysis shows that the most probable dimer and spacing between dimers for InGaAs and InAs are the same (8.4 Å). However, the distribution of dimer spacing is broader for InGaAs, and the second most common spacing is 12.6 Å. Several possible dimer and spacing structures are shown in Fig. 3.3(e).
Figure 3.3. The experimentally observed distribution of dimer lengths and spacings between dimers on InAs and InGaAs surfaces from 77 K LT-STM data. (a) InGaAs dimer length distribution. (b) InGaAs spacing distribution. (c) InAs dimer length distribution. (d) InAs spacing distribution. (e) Possible InAs and InGaAs dimer and spacing structures. The most probable surface structures for InAs and InGaAs are almost identical; however, InGaAs has broader dimer spacing distribution.
The phase transition between the RT (4×2) reconstruction and the LT reconstruction is reversible because the surface reconstructions are observed in both the transition from RT to LT and the transition from LT to RT directions. It is noted contaminants can be excluded from causing the LT reconstruction because (a) the RT surface structure can be recovered by heating the LT structure to RT; (b) the pressure in the STM chamber is below 1×10^{-10} Torr during cooling and LT imaging; (c) physisorbates rarely make ordered structures [20].

Figure 3.4. Scanning tunneling spectroscopy for the following group III rich In_{0.53}Ga_{0.47}As(001)-(4×2) surfaces. (a) Clean n-type surface. (b) Clean p-type surface. For clean surfaces, the Fermi level (0 V) lies between the valence band (VB) and midgap for n-type, and near the VB for p-type. These results are based on statistical analysis of more 15 samples/STM tips.
3.4.1.3. Electronic Properties of In$_{0.53}$Ga$_{0.47}$As Surface

Scanning tunneling spectroscopy (STS) was used to determine the electronic properties of the surface. In STS, the tip is placed above the surface, and the tunneling current $I(V)$, along with its first derivative $dI/dV$ spectrum, is measured as a function of the tip-sample voltage. The positions of the band edges relative to 0 V (Fermi level) are used to determine the Fermi level position. Figures 3.4(a) and 3.4(b), show STS spectra of the clean $n$-type and $p$-type In$_{0.53}$Ga$_{0.47}$As(001)-(4×2) surfaces at RT. These $dI/dV$ curves were acquired at 15-20 different spots on the same surface for both $n$-type and $p$-type samples; afterwards, they are averaged to get STS results shown in Fig. 3.4. For each curve, one bandgap value and distance of Fermi level position relative to CBM or VBM are obtained. The experiments were repeated on 15 different samples using different tips to get the average value and standard deviation of Fermi level position relative to CBM or VBM. For clean $n$-type samples, the Fermi level should reside near the conduction band (CB) for an unpinned dipole-free surface. However, the STS spectra on over 15 samples/STM tips shows that for $n$-type In$_{0.53}$Ga$_{0.47}$As(001)-(4×2) surface, the Fermi level resides between the midgap and the valence band (VB) (0.31 ± 0.18 eV close to VB). The Fermi level shift may be caused by surface band bending or by gap states; a surface dipole may exist due to differences in the number of filled and empty dangling bonds on the surface or from surface defects; a more detailed discussion can be found in ref. [38]. For $p$-type In$_{0.53}$Ga$_{0.47}$As(001)-(4×2) surface, the Fermi level resides near the VB (0.26 ± 0.09 eV close to VB) which is typical for unpinned dipole-free surface but also consistent with a surface dipole or the pinning states near the VB.
3.4.2. Density Functional Theory Results

In order to understand the difference in the surface reconstruction between 300 K and 77 K on In$_{0.53}$Ga$_{0.47}$As(001), DFT calculations were performed on a series of structure models. In Fig. 3.5, five possible structures for the group III rich In$_{0.5}$Ga$_{0.5}$As(001)-(4×2) surface are shown along with their energy differences relative to the lowest total energy case (undimerized-buckled). Double unit cells are employed because of the large unit cell observed in the low temperature surface reconstruction. The criteria to distinguish all of these structures are whether the row is dimerized, undimerized or mixed, and whether the trough dimers are buckled or unbuckled. For example, the mixed-buckled structure consists of one In/Ga dimer and two undimerized In/Ga atoms in the row, and one buckled In/Ga dimer plus three unbuckled In/Ga dimers in the trough per double (4×2) unit cell. The undimerized-buckled structure consists of four undimerized In/Ga atoms in the row, and two buckled In/Ga dimers plus two unbuckled In/Ga dimers in the trough per double (4×2) unit cell. The main difference between the mixed-buckled structure and the undimerized-buckled structure is that for each double (4×2) unit cell, mixed-buckled structure has one row In/Ga dimer in the topmost layer and one buckled dimer in the trough, while undimerized-buckled structure has no row dimers and two buckled dimers in the trough. The relative energy differences in Fig. 3.5 are the total energy differences per double (4×2) unit cell. The dimerized-unbuckled and the undimerized-unbuckled structures, and their energy DFT calculations are based on a single unit cell, and, subsequently, extended into a double unit cell since there is no relaxed structure found with unbuckled In/Ga dimers in the trough for a double unit cell calculation. The other two cases (mixed-buckled and undimerized-
buckled structures) are based on a double unit cell. For mixed-unbuckled case, a relaxed stable structure was not obtained. The mixed-unbuckled energy shown in Fig. 3.5(a) is estimated based on the DFT calculated energies of dimerized-unbuckled and undimerized-unbuckled structures. From the relative energies in Fig. 3.5 of the dimerized-unbuckled and the undimerized-unbuckled structures, the dimerization energy for In$_{0.5}$Ga$_{0.5}$As(001)-(4×2) surface is estimated to be zero so the mixed-unbuckled energy is estimated to be degenerate with the dimerized-unbuckled and the undimerized unbuckled energies. Spin-polarization effects were also investigated, but spin-polarization did not affect the relative total energies.
Figure 3.5. Summary of possible surface structures for InGaAs(001) according to DFT calculations. Only the top atomic layers are shown for clarity of presentation. (a) Mixed-unbuckled structure. (b) Undimerized-unbuckled structure. (c) Dimerized-unbuckled structure. (d) Mixed-buckled structure. (e) Undimerized-buckled structure. Double unit cells are employed because of the large unit cell observed in the low temperature surface reconstruction. The dimerized-unbuckled and undimerized-unbuckled structures, and corresponding DFT calculation are based on a single unit cell which was extended into a double unit cell since a relaxed structure with unbuckled In/Ga dimers in the trough for a double unit cell could not be found. A single (4×2) unit cell is indicated in undimerized-unbuckled [Fig. 3.5(b)] and dimerized-unbuckled structures [Fig. 3.5(c)]. Other two InGaAs cases (mixed-buckled and undimerized-buckled structures) are based on a double unit cell. The energies shown in the figure is their energy differences relative to the lowest total energy case (undimerized-buckled). Buckled atoms in the upward position are highlighted with up symbol. Note Fig. 3.5(a) is not relaxed structure.
(a) Mix-unbuckled
E = 1.18 eV

(b) undimerized-unbuckled
E = 1.18 eV

(c) dimerized-unbuckled
E = 1.17 eV

(d) Mix-buckled
E = 0.38 eV

(e) Undimerized-buckled
E = 0 eV
3.4.2.1. Trough Structure

According to the DFT calculations, structures with highly buckled trough dimers are predicted to be more stable than structures with only tilted trough dimers by at least 0.79 eV for InGaAs and 0.52 eV for InAs [20] per double unit cell. It is noted that the symmetry of the buckling in the trough is slightly different for the InGaAs(001)-(4×2) undimerized-buckled structure than the symmetry for the buckling in the trough for InAs(001)-(4×2) presented in ref. [20] because of the propensity of In atoms to be in the up position. Two other highly buckled trough dimers structures with different buckling directions were also investigated, but buckling direction did not affect the total energies by more than 0.03 – 0.08 eV. The height difference between buckled and unbuckled dimers is around 1.2 – 1.3 Å. However, experimentally there is no strong evidence showing that the trough is buckled for InAs at both 300 K room temperature and 77 K low temperature [20]. For InAs, there are three experimental observations which strongly argue against the existence of extreme buckling in the trough: (a) STM image at 77 K of the trough clearly shows trough dimers without buckling; (b) the 77 K experimental structure clearly has mixed dimerized and undimerized In atoms on the row in contrast to the lowest energy structure calculated by DFT with buckled trough dimers; (c) the experimental reconstruction changes between 77 K and 300 K, but the DFT energy difference between mixed-buckled and undimerized-buckled InAs structures are more than 0.61 eV per double (4×2) unit cell which is inconsistent with the experimentally observed switch in reconstruction between 77 K and 300 K. Therefore, the extremely buckled structures were considered highly unlikely as possible structures for the InAs (001) surface. It was hypothesized that the DFT was not in agreement with the
experiments for the trough structure because of the limited cell size employed in DFT could not reproduce the strain in a real system with limited terrace size and surface defects. However, it is noted that even though buckled trough atoms were not observed at 77 K on InAs(001)-(4×2), it is possible that the atoms in the trough are still fluctuating between buckled and unbuckled positions at 77 K.

For InGaAs case, there is no trough resolution at 300 K nor at 77 K but again three arguments apply: (a) The difference in height observed by STM between the row and trough is 1.2 to 1.5 Å at both 77 K and 300 K on both InAs(001)-(4×2) and InGaAs(001)-(4×2); this is consistent with the InAs(001)-(4×2) and InGaAs(001)-(4×2) having the same trough structures. This height does not match the difference in height between the relaxed row In/Ga atoms and unbuckled trough atoms in the DFT calculations (2.3 Å), but the same issue was observed with InAs(001)-(4×2) and is presumed to be due to the highly perturbed electronic structure of the trough atoms. (b) The 77 K experimental structure clearly has mixed dimers on the row in contrast to the lowest energy structure calculated by DFT with buckled trough dimers. (c) The experimental reconstruction changes between 77 K and 300 K, but the DFT energy difference between mixed-buckled and undimerized-buckled InGaAs structures are more than 0.38 eV per double (4×2) unit cell which is inconsistent with the experimentally observed switch in reconstruction between 77 K and 300 K. All the calculations shown in Fig. 3.5 assume that In/Ga atoms have equal distribution on the InGaAs surface. Since it is known that the InGaAs surface can be enriched in indium due to surface segregation [39], the DFT calculations were also run with only In atoms in the topmost layer. The energy differences between these cases were similar to the non-In enriched surface.
When the surface layer consists of only indium atoms, there is still buckling in the trough consistent with the buckling not being an artifact of the choice of a regular polymorph for InGaAs. The difference between experiment and theory for unbuckled and buckled is probably due to the inability of the small slab to capture the proper strain relaxation of the experimentally observed surface which has terraces sizes well over 10 - 100 \times larger than the double unit cells employed in these calculations.

3.4.2.2. Row Structure

For the other three structures: dimerized-unbuckled, undimerized-unbuckled and mixed-unbuckled, since the trough structures remain same, the main difference lies on the row structure. For unbuckled InGaAs(001) surface, the dimerization energy is about 0 eV. All three unbuckled InGaAs(001) reconstructions are energetically degenerate.

Figure 3.6. DFT molecular dynamics (MD) model of the row structures of InGaAs clean surface annealed at 900 K at different annealing times in femtoseconds (fs). Bond angles for atomic positions are calculated to assist in determining the mechanisms of row dimers formation and breaking. The normal to the paper is the z direction.

A DFT molecular dynamics (MD) study was performed to determine if the surface row fluctuates between the dimerized structure (mixed-unbuckled) and the
undimerized structure (undimerized-unbuckled) at elevated temperature. In these calculations, the trough dimers (8 In/Ga atoms) and 12 adjacent to them As atoms were fixed in the z direction in the nearly flat positions of the dimerized-unbuckled relaxed structure to provide a realistic simulation of the experimentally observed structures; all other surface and subsurface atoms were free to move except the bottom three layers which were always fixed in their bulk-like positions. The InGaAs sample was DFT annealed at 900 K for 1000 fs with a 1.0 fs time steps. The elevated temperature was employed instead of 300 K to reduce the number of time steps required to simulate dimer breaking and formation. The results were checked by doing simulations at a second elevated temperature (1200 K). Fig. 3.6 shows the row structures of InGaAs clean surface annealed at 900 K at different annealing times (fs). The 125 fs and 126 fs snapshots are the transition structures before and after row dimer breaking. The 324 fs and 325 fs snapshots are the transition structures before and after row dimer formation. The 779 fs and 780 fs snapshots are the transition structures before and after row dimer re-breaking. These results clearly show that surface row dimers can spontaneously break their dimer bonds and switch back to form dimer bonds between three unbuckled structures since the total energy difference is so small. In a simple Arrhenius model, since the formation/breaking time is 260 fs at 900 K, the formation/breaking time should be about 2 ps at 300 K. The estimated 300 K fluctuation time is faster than the STM scanning time (around 100 ms) consistent with a 300 K surface showing an undimerized-unbuckled surface structure due to a thermal superposition of dimerized-unbuckled, undimerized-unbuckled and mixed-unbuckled structures since undimerized row structures have higher symmetry.
A detailed analysis of the annealing calculation shows the mechanism of rapid dimer formation and breaking. In the initial structure (0 fs), the row is mixed with one In/Ga dimer and two undimerized In/Ga atoms. The bond angles between edge As atoms and row In/Ga atoms are different for the undimerized and dimerized structures. For the undimerized structure, the bond angles are between 166° to 178°, consistent with sp hybridization. For dimerized structure, the bond angles are between 138° to 143° consistent with a strained sp² hybridization since these bond angles are slightly larger than the ideal 120° for sp² hybridized system. At 125 fs, As atoms 5, 6 and their neighboring row Ga atom move in the positive x direction, and As atoms 7, 8 and their neighboring In atom move in the negative x direction. The bond length between the dimerized In and Ga atoms is expanded from 2.79 Å (0 fs, dimerized In/Ga atoms) to 3.16 Å (125 fs). This twist bending mode makes this row dimer break.

At 324 fs, As atoms 1, 2, 3, 4 and the undimerized neighboring row In/Ga atoms all are moving in the negative x direction. At 324 fs, these In/Ga atoms are also moving upwards in the z direction increasing their bond angles with the row edge As atoms to 126° - 128° thereby forming a sp² geometry which allows row dimer formation. Simultaneously, the bond length between these Ga and In atoms becomes shorter, from 4.20 Å (0 fs, undimerized In/Ga atoms) to 3.10 Å (324 fs). The initial row bond formed at 324 fs is not completely relaxed; at 388 fs, the In/Ga atoms are closer (2.48 Å). After 388 fs, the In/Ga atoms bond length becomes larger and the upper row dimer start to break. At 779 fs, the upper row In/Ga dimer bond length is 3.17 Å, and these In/Ga are moving back close to the initial structure (0 fs, undimerized In/Ga atoms) in the z direction causing the bond angle to increase and thereby breaking the dimer at 780 fs.
In summary, three ways to form or break the row dimers were observed in the DFT-MD simulations: (a) as shown in the 125 fs diagram, a large twist and bend greatly elongates an In/Ga dimer bond thereby breaking a dimer bond; (b) as shown in the 324 fs diagram, an In/Ga upwards z direction motion decreases the bond angles from sp to sp$^2$ thereby forming a dimer bond; (c) as shown in the 779 fs diagram, In/Ga downwards z direction motion increases the bond angles from sp$^2$ to sp thereby breaking a dimer bond.

77 K STM experimental results strongly suggest that the most probable row structure for InGaAs is mixed row structure, which consists of one In/Ga dimer and two undimerized In/Ga atoms in the row per double unit cell. However, there is another probable row structure for InGaAs surface (12.6 Å) shown in Fig. 3.3. This is similar to Ge(001)-(2×1) cases at RT and LT [36]. At RT, In/Ga atoms in the top layer fluctuate between the dimerized structure and the undimerized structure. At LT, the surface atoms are frozen. The same DFT-MD study was performed on InAs(001)-(4×2) using the identical DFT parameters employed for InGaAs(001)-(4×2). Again at 900 K, starting with an initial mixed row structure and flat trough dimers, row dimer breaking and formation was observed on within the 1000 fs simulation time. The mechanisms of row dimer formation and breaking were almost identical, the extreme motion of row edge As atoms increasing the In-In dimer bond length weakening the In-In bond, z motion induced changes in bond angles, and extreme dimer bond lengthening. These results are consistent with the 300 K InAs(001)-(4×2) structure also being a thermal superposition (see Appendix A).
3.4.2.3. Density of States

The density of states (DOS) of dimerized-unbuckled, mixed-buckled, and undimerized-buckled structures have been studied to identify the source of the Fermi level pinning. DOS was calculated and shown in the bandgap region. Both mixed and undimerized-buckled structures contain row In/Ga atoms making only two bonds with row edge As atoms; these atoms are sp hybridized in contrast to nearly all other III-V surface reconstructions except InAs(001)-(4×2) [20]. The atoms are considered sp hybridized due to their coordination to two atoms while having close to 180° bond angles. It is surprising to find stable sp hybridized atoms on a group III rich surface since all other known surface reconstructions have only sp\(^2\) and sp\(^3\) hybridized atoms on the surfaces. These sp hybridized In/Ga atoms may have dangling bonds which pin the Fermi level. Fig. 3.7(c) shows the DOS results of the clean undimerized-buckled In\(_{0.5}\)Ga\(_{0.5}\)As(001) surface. There is a reasonable bandgap containing no states for undimerized-buckled structure. This shows that the sp hybridized atoms do not pin the Fermi level.
Figure 3.7. DFT relaxed atomic structures and density of states (DOS) curves for group III rich In\textsubscript{0.5}Ga\textsubscript{0.5}As(001) reconstructions. The dimerized-unbuckled and mixed-buckled structures have no bandgap, and the surfaces are pinned. The undimerized-buckled structure has a bandgap, and the surface is unpinned.
The trough dimers are a likely source of the Fermi level pinning since they are in a strained atomic geometry. Each of the tricoordinated In/Ga atoms in the trough has an empty dangling bond so the relaxed geometry would be triangular planar $sp^2$ bonding; instead, in the unbuckled geometry from the DFT model, the trough In/Ga atoms are in a tetrahedral $sp^3$ geometry. Buckling of the trough In/Ga dimer allows the dimer atom in the down position to have a more $sp^2$ bonding geometry while placing the dimer atom in the upward position to be in a more $sp^3$ bonding geometry; this would be unstrained if there was charge transfer to the atoms in the upward position to fill their dangling bonds. As shown in Fig. 3.7, for unbuckled and mixed-buckled structures, there is no bandgap consistent with the strained unbuckled trough dimers or the row dimers in these reconstructions pinning the Fermi level.
Figure 3.8. 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 eV and +0.25 eV; the contour spacing is $5 \times 10^{-3}$ eÅ$^{-3}$. (b) The undimerized-buckled structure with the band edge filled states charge density summed between -0.5 eV and 0 eV (Fermi level $E_F = 0$ eV); the contour spacing is $1 \times 10^{-2}$ eÅ$^{-3}$. (c) The undimerized-buckled for band edge empty states with the charge density summed between 0 eV and +0.5 eV; the contour spacing is $2 \times 10^{-3}$ eÅ$^{-3}$. The charge density is in blue. The buckled atoms in the upward position are highlighted with up symbol in the third column. For the top view and the Bader charge view, only the top three atomic layers are shown. For the Bader charges, the relative charge differences are shown. The relative charge differences are calculated from differences between surface atoms and bulk atoms.
To identify whether the strained unbuckled trough dimers or the row dimers, or both of them pin the Fermi level, the band-decomposed electron charge densities for the mixed-buckled and the undimerized-buckled structures are calculated and plotted in Fig. 3.8. The bandgap states are visualized by calculating and summing band-decomposed charge density between -0.25 eV to 0.25 eV for the pinned mixed-buckled structure; the valence band edge states are visualized by calculating and summing the band-decomposed charge density between -0.5 eV and 0 eV (with Fermi level $E_f = 0$ eV) for the unpinned undimerized-buckled structure; the conduction band edge states are visualized by calculating and summing the band-decomposed charge density between 0 eV and + 0.5 eV for the unpinned undimerized-buckled 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. 3.8(a). 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 undimerized-buckled structure, the buckling of the trough dimers relieves the stress and unpins the surface. The filled valence band edge state distribution for undimerized-buckled structure is localized on the buckled In/Ga atoms in the trough and while the empty conduction band edge states are localized on the undimerized In/Ga atoms in the row.

A top view of the undimerized-buckled band edge filled states from -0.5 eV to 0 eV and empty states from 0 eV to + 0.5 eV show there is only empty orbital overlap between the sp In/Ga atoms consistent with the row sp In/Ga atoms forming π bonding with the row edge As atoms instead of forming partially filled dangling bonds.
Since the 300 K data is expected to be a superposition of isomers of the three unbuckled structures, DFT predicts a pinned Fermi level for the clean In$_{0.5}$Ga$_{0.5}$As(001) surface consistent with the data. To better understand the mechanism of the pinning by the unbuckled trough dimers, the Bader charges on all the surface atoms were calculated [40-42]. The Bader charges of atoms are obtained by spatial decomposition of 3D field of converged electron density to regions centered at particular atoms and subsequent charge density integration within these regions. The 3D charge density field is decomposed to atomic regions by performing a gradient analysis and finding zero-flux surfaces around atoms. The Bader charge approach provides much more meaningful and physically correct charge calculation for plane-wave DFT calculations than charge density integration within spherical regions of empirical atomic radii. Note, that a Bader charge having a positive value indicates number of valence electrons associated with a particular atom. In the present simulations, positive Bader charge differences indicate increasing of the electron charges associated with the atoms, which makes the atoms more negatively charged. The relative charge differences are calculated from Bader charge differences between surface atoms and bulk atoms. For example, the tricoordinated row edge As atoms lose electrons compared to bulk As atoms so they are shown with negative changes in Bader charge in Fig. 3.8.

In Fig. 3.8, the results show all the surface atoms have close to bulk-like charge for both mixed-buckled and undimerized-buckled structures, and the largest charge transfer is only ~ 0.3 electrons for any of the surface atoms. Comparing Bader charges between mixed-buckled (pinned structure) and undimerized-buckled (unpinned structure), in the unpinned undimerized-buckled structure, two row In/Ga atoms in the lower half of
the row lose a total of 0.19 electrons, the four As atoms at the edge of row lose a total of 0.24 electrons, and the In/Ga dimer in the lower left of the trough gains 0.2 electrons. The breaking of the row dimers bonds induces a buckling of one of the trough dimers, and the buckling causes a charge transfer of about 0.2 electrons to the trough dimer which partially fills the dangling bond on the buckled trough atoms partially relieving the strain. In essence, the unpinning is accompanied by a small charge transfer from the rows to the buckled trough dimer stabilizing the atom in the sp$^3$ buckled up position. This is consistent with the buckled trough dimers being unpinned and the unbuckled trough dimers being pinned as shown by the bandgap states in Fig. 3.7(a). Although the DFT model is consistent with the STS data, it is noted that the high density of surface defects may affect the experimental electronic properties of In$_{0.5}$Ga$_{0.5}$As(001)-(4×2).

3.5. Conclusions

STM images of the decapped group III rich In$_{0.53}$Ga$_{0.47}$As(001) surface reconstruction have been obtained at both 300 K and 77 K. Empirically, the STM results are consistent with different surface reconstructions. At 300 K, STM images show that the In$_{0.53}$Ga$_{0.47}$As(001) surface reconstruction is comprised of undimerized In/Ga atoms in the top layer. Conversely, 77 K STM images show that the In$_{0.53}$Ga$_{0.47}$As(001) surface reconstruction is primarily comprised of one In/Ga dimer and two undimerized In/Ga atoms in the top layer in a double (4×2) unit cell. STS results show that for clean 300 K surfaces, the Fermi level resides between the valence band (VB) and midgap for n-type, and near the VB for p-type consistent with the RT surface being either pinned or having a large surface dipole. DFT molecular dynamics (MD) simulations show that the 300 K
structure is not a unique structure distinct from the 77 K structure but instead the experimentally observed 300 K structure is consistent with a thermal superposition of three structures including the 77 K structure. DFT-MD showed the row dimer formation and breaking is facilitated by the very large motions of tricoordinated row edge As atoms and z motion of In/Ga row atoms induced changes in As-In/Ga-As bond angles at elevated temperature. DFT calculations of the band-decomposed charge density indicate that the strained unbuckled trough dimers being responsible for the surface pinning.

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Chapter 3, in full, has been accepted for publication of the material as it appears in J. Shen, J. B. Clemens, E. A. Chagarov, D. L. Feldwinn, W. Melitz, T. Song, S.R. Bishop, R. Droopad, and A. C. Kummel, Structural and electronic properties of group III rich In\textsubscript{0.53}Ga\textsubscript{0.47}As(0 0 1), Surface Science (2010). The dissertation author was the primary investigator and author of this paper.
Figure 3.9. Row structures of InAs clean surface annealed at 900 K at different annealing times in femtosecond (fs). Bond angles for atomic positions are calculated to assist in determining the mechanisms of row dimers formation and breaking. The normal to the paper is the z direction.

A DFT molecular dynamics (MD) study for InAs surface was performed to determine if the surface row fluctuates between the dimerized structure (mixed-unbuckled) and the undimerized structure (undimerized-unbuckled) at elevated temperature. In these calculations, the trough dimers (8 In atoms) and 12 adjacent As atoms were fixed in the z direction in the nearly flat positions of the dimerized-unbuckled relaxed structure to provide a realistic simulation of the experimentally observed structures; all other surface and subsurface atoms were free to move except the bottom three layers which were always fixed in their bulk-like positions. The InAs sample was DFT annealed at 900 K for 1000 fs with 1.0 fs time steps. The elevated temperature was employed instead of 300 K to reduce the number of 1 fs time steps required to simulate dimer breaking and formation. Fig. 3.9 shows the row structures of InAs clean surface.
annealed at 900 K at different annealing times (fs). The 355 fs and 356 fs snap shots are the transition structures before and after upper row dimer formation. The 459 fs and 460 fs snap shots are the transition structures before and after lower row dimer breaking. The 975 fs and 976 fs snap shots are the transition structures before and after upper row dimer breaking. The results show that all of three structures: mixed-unbuckled, undimerized-unbuckled and dimerized-unbuckled are observed during 900 K InAs DFT-MD even in a short time period.

In a simple Arrhenius model, since the formation/breaking time is 325 fs at 900 K, the formation/breaking time should be about 3 ps at 300 K. The estimated 300 K formation/breaking time is faster than the STM scanning time (around 100 ms). This is consistent with a 300 K surface showing an undimerized-unbuckled surface structure in STM imaging due to a thermal superposition of dimerized-unbuckled, undimerized-unbuckled and mixed-unbuckled structures since undimerized row structure has higher symmetry.

A detailed analysis of the annealing calculation shows the mechanism of rapid dimer formation and breaking. In the initial structure (0 fs), the row is mixed with one In dimer and two undimerized In atoms. The bond angles between edge As atoms and row In atoms are different for the undimerized and dimerized structures. For the undimerized structure, the bond angles are between 166° to 179°, consistent with sp hybridization. For the dimerized structure, the bond angles are between 138° to 142° consistent with a strained sp$^2$ hybridization. The angles are almost identical to InGaAs surface.

At 355 fs, the upper two undimerized neighboring row In atoms are moving upwards in the z direction decreasing their bond angles with the edge row As atoms 1, 2,
3, 4 to 143° - 150° comparing to original bond angles 166° - 179°. Simultaneously, the bond length between these two In atoms becomes shorter, from 4.36 Å (0 fs, undimerized In atoms) to 3.41 Å (355 fs) causing dimer bond formation.

At 459 fs, As atom 8 and both the lower two dimerized neighboring row In atoms are moving in negative x direction while As atom 6 remains in the same x position causing the bond length between As atom 6 and In atom to increase from 2.73 Å (0 fs) to 3.15 Å (459 fs). As atom 5 is moving in positive y direction and As atom 7 is moving in negative y direction, which makes the bond length between the dimerized In atoms expand from 2.90 Å (0 fs, dimerized In atoms) to 3.41 Å (459 fs). Therefore, simultaneous, the In-In bond and one In-As bond are being severely elongated; since the In-As bond is stronger, the In-In dimer bond breaks.

At 975 fs, As atoms 1, 2, 3, 4 and the upper two dimerized neighboring row In atoms are moving back close to the initial structure (0 fs, undimerized In atoms) in the z direction causing the bond angle to increase thereby breaking the dimer at 976 fs. The upper row In dimer bond length is 3.41 Å.

In summary, three ways to form or break the In row dimer were observed in the DFT-MD simulation: (a) as shown in the 356 fs diagram, extreme upwards motion of the upper two row In atoms causes the As-In-As bond angles to decrease to an sp² geometry forming the In-In dimer bond; (b) as shown in the 460 fs diagram, the extreme motion of row edge As atoms increases the In-In dimer bond length weakening the In-In bond, (c) as shown in the 976 fs diagram, extreme downwards motion of the upper two row In atoms causes the As-In-As bond angles to increase to an sp geometry thereby inducing breaking of a row dimer bond.
Figure 3.10. LEED images of the group III-rich $\text{In}_{0.53}\text{Ga}_{0.47}\text{As}(001)$-(4×2) and $\text{InAs}(001)$-(4×2) surface at 300 K.

LEED results show that InAs and InGaAs have same pattern, which means InAs and InGaAs have same surface reconstruction.

References


Chapter 4

Bonding Geometries at the In$_2$O and SiO/III-V Semiconductor Interface

4.1. Abstract

Oxide monolayers and submonolayers formed by vapor deposition of In$_2$O and SiO oxides on InAs(001)-(4×2) were studied by scanning tunneling microscopy (STM). At low coverage, In$_2$O molecules bond to the edges of the rows and most likely form new In-As bonds to the surface without any disruption of the clean surface structure. Annealing the In$_2$O/InAs(001)-(4×2) surface to 380°C results in formation of flat ordered monolayer rectangular islands. The annealed In$_2$O no longer bonds with just the As atoms at the edge of row but also forms new O-In bonds in the trough. SiO chemisorption on InAs(001)-(4×2) is completely different than In$_2$O chemisorption. At room temperature, even at low coverage SiO adsorbates bond to themselves and form nanoclusters. For SiO/InA(001)-(4×2) post-deposition annealing (PDA) does not disperse the nanoclusters into flat islands. Both In$_2$O and SiO depositions on InAs(001)-(4×2) surface do not displace surface atoms during both room temperature deposition and post-deposition annealing.

4.2. Introduction

The current silicon based integrated circuits (IC) technologies have dominated the high-performance logic industry for decades. The success with the semiconductor IC industries lies in device downsizing: scaling. However, continuing the scaling is becoming increasingly difficult, and silicon transistor technology is rapidly approaching
its physical limits. According to the 2008 updated International Technology Roadmap for Semiconductors (ITRS) [1], to attain adequate drive current for highly scaled metal-oxide semiconductor field-effect transistors (MOSFETs), eventually other high transport channel materials (Ge and III-V) are needed for beyond 22 nm node generation so that semiconductor industries can continue keeping Moore’s Law.

Recently, extensive studies have been carried out on III-V compound semiconductors for potential channel materials of MOSFETs [2-4]. Several academic and industry groups have shown promising III-V MOSFETs results [5-12]. However, the interface between oxides and III-V semiconductors is not well understood. Forming electrically passive interfaces between the gate oxide and the channel [13] is still a major issue for the development of MOSFETs devices. Unlike hydrogen passivated silicon and SiO₂ interfaces (D_{it} \sim 10^{10} \text{eV}^{-1} \text{cm}^{-2}) [14], oxide/III-V interfaces have large interfacial trap densities, D_{it} between 10^{12} and 10^{14} \text{eV}^{-1} \text{cm}^{-2} [15-16], so enhancement mode III-V MOSFETs devices require very high capacitance even to counteract the lowest reported the interfacial trap densities. In order to obtain a fundamental understanding of surface passivation of III-V compound semiconductors, it is critical to investigate and understand surface morphological evolution and the oxide/semiconductor interface bonding at the atomic level in order to facilitate gate oxide selection for III-V MOSFETs device and enable very aggressive oxide scaling.

InAs is an attractive channel material for high speed, low power MOSFET due to its very high effective electron mobility (~ 15,000 cm² V⁻¹ s⁻¹) compared to Si (~300 cm² V⁻¹ s⁻¹) at 300 K [17]. InAs FET results have shown there is potential for high performance InAs based MOSFET [18,19]. This report is focused upon the c(8×2)/(4×2)
surface since other surfaces like As-rich (2×4) reconstruction readily undergo oxygen induced displacement reactions [20-23]. Although InAs(001) [24-26] have been the focus of many scanning tunneling microscopy (STM) studies, only one STM study has been performed on the bonding geometry of oxide on InAs(001) surface [27].

To develop an atomic understanding of oxide morphologies on InAs(001)-c(8×2)/(4×2), the bonding geometries of two different oxides In$_2$O and SiO on InAs(001)-c(8×2)/(4×2) were investigated. Scanning tunneling microscopy (STM) was used to determine the exact interfacial bonding geometries of In$_2$O and SiO/InAs(001)-c(8×2)/(4×2) after room temperature oxide deposition. In addition, the effects of post-deposition annealing on oxide bonding sites were investigated. The results are focused on InAs, but the results are readily applied to InGaAs systems due to similar surface structure and oxide bonding geometry [28].

4.3. Experimental and Computational Methods

MBE was employed to grow 0.2 μm of 1×10$^{18}$ cm$^{-3}$ doped InAs layer on 500 μm thick InAs(001) substrates with 1×10$^{18}$ cm$^{-3}$ doping. Experiments were performed on both n-type and p-type wafers. The re-grown wafers were capped in situ with a 50 nm protective arsenic cap. The wafers were transferred to a vacuum container for transporting to the STM chamber. Experiments were performed in two ultrahigh vacuum (UHV) chamber systems with base pressures of 2×10$^{-10}$ Torr. Each chamber was equipped with low energy electron diffraction (LEED) and either a Park Scientific room temperature or an Omicron variable temperature (VT) STM. The InAs(001)-
(8×2)/(4×2) surface was prepared by thermal decapping method. Details concerning the decapping method used in this study have been discussed elsewhere [28,29].

After the (8×2)/(4×2) surface reconstruction was verified by LEED, the sample was transferred to the STM chamber, where STM measurements were performed at room temperature. All of the STM measurements were carried out at room temperature (RT) using electrochemically etched tungsten tips. The InAs(001)-c(8×2)/(4×2) clean surfaces could be observed with both filled and empty state STM. Subsequently, In$_2$O or SiO was deposited in the main chamber by evaporating sintered In$_2$O$_3$(s) (Aldrich Chem. Co.) or SiO(s) (Alfa Aesar) from a high temperature effusion cell (Applied EPI) contained in a differentially pumped chamber. In$_2$O$_3$(s) sublimates as In$_2$O (g) and O$_2$ (g) at 1000 - 1025 °C [30]. However due to the low sticking probability of O$_2$ on group III-rich c(8×2)/(4×2) surfaces [31], the majority of the adsorbed species are In$_2$O. SiO(s) evaporates congruently as SiO(g) molecules at 950 - 975 °C [29]. During evaporation, the main chamber pressure is 2×10$^{-7}$ Torr or 5×10$^{-9}$ Torr for In$_2$O and SiO, respectively.
Figure 4.1. Structure of clean InAs(001)-(4×2) at 300 K. (a) A filled state (Vs = -2 V, It = 0.2 nA, 2000 Å × 2000 Å) STM image obtained from the InAs(001)-(4×2) clean surface. (b) A high resolution filled state (Vs = -2 V, It = 0.2 nA, 100 Å × 85 Å) STM image obtained from the InAs(001)-(4×2) clean surface. (c) Ball-and-stick diagram of the InAs(001)-(4×2) reconstruction. The atomic InAs(001)-(4×2) reconstruction structure model has been discussed in Ref. 22. The green rectangle presents the unit cell of c(8×2). Note that In atoms on the row are undimerized, and the In row atoms have the same height as the As atoms at the edge of row.
4.4. Results and Discussion

In-rich InAs(001)-(4×2) can readily be prepared by decapping of As$_2$ capped InAs(001) wafers. A typical STM image of a clean InAs(001)-c(8×2)/(4×2) surface prepared by decapping method can be seen in Fig. 4.1(a). All STM images in this study were taken with a negative sample bias using the constant-current tunneling mode. The InAs(001)-(4×2) surface has a unit cell consisting of two undimerized group III atoms on the row and two group III homodimers in the trough. Details of the InAs(001)-(4×2) clean surface structure are discussed elsewhere [26].

Figure 4.2. Bonding of RT deposited In$_2$O/InAs(001)-(4×2). (a) A filled state ($V_s = -1.5$ V, $I_t = 0.2$ nA, 35 Å × 35 Å) STM image obtained from the InAs(001)-(4×2) surface with ~ 25% coverage of In$_2$O. (b) Possible atomic bonding structure diagrams of In$_2$O/InAs(001)-(4×2) surface along single In$_2$O chemisorption bonding sites with top view (upper) and side view (lower). Note that this image is taken in the Park Scientific RT-STM system.
4.4.1. Indium Monoxide (In\textsubscript{2}O)

Once the surface structure of InAs(001)-(4×2) was characterized, the gate oxides were deposited to investigate the exact atomic bonding structures of gate-oxide/III-V interfaces. STM results showed that the initial deposited In\textsubscript{2}O molecules bond to the edges of the rows and most likely form new In-As bonds to the surface without any disruption of the clean surface structure, shown in Fig. 4.2(a). In filled state STM images, In\textsubscript{2}O is imaged as a bright feature on the clean InAs(001)-(4×2) surface. Figure 4.2(b) shows a structural model illustrating the possible oxide bonding structure for room temperature deposition. Density function theory (DFT) results shows the binding energy is 0.84 eV/In\textsubscript{2}O for InAs surface [28]. The binding energy [32] was calculated by subtracting the total energy of the most stable clean surface structure and gas phase oxide molecule from the total energy of the oxide/InAs complex:

\[ E_{\text{bind}}^{\text{oxide/InAs}} = E_{\text{oxide/InAs}} - (E_{\text{InAs}} + E_{\text{oxide}}), \]

where \( E_{\text{bind}}^{\text{oxide/InAs}} \) is the binding energy between oxide molecules and InAs surface, \( E_{\text{oxide/InAs}} \) is the total energy of oxide deposited InAs double unit cell slab, \( E_{\text{InAs}} \) is the total energy of the clean InAs double unit cell slab, and \( E_{\text{oxide}} \) is the total energy of free oxide molecules [28].
Figure 4.3. Height analysis for RT deposition of In$_2$O/InAs(001)-(4×2). (a) Height distribution of only the oxide-free regions of the In$_2$O/InAs(001)-(4×2) surface in Fig. 4.2(a). (b) Height distributions of the entire In$_2$O/InAs(001)-(4×2) surface in Fig. 4.2(a). There are two position peaks corresponding clean surface region and oxide covered surface region. The distance between two peaks is 1.5 Å. Inset in Fig. 4.3a is an expanded height distribution of In$_2$O deposited surface at the higher height region that reveals distinct second layer growth.

A height distribution analysis was performed to determine the room temperature growth mechanism. At medium coverage (~25% monolayer), the In$_2$O formed islands that are in the [110] direction as shown in Fig. 4.2(a). Prior to all the first layer bonding sites being occupied with oxides, distinct second layer growth is observed on the oxide
for room temperature oxide deposition. For only clean surface region, there is height distribution peak near 7.0 Å, shown in Fig. 4.2(a). For the whole surface, there is a bimodal height distribution shown in Fig. 4.3(b) with a lower position peak which is identical to the clean region height distribution of the InAs(001)-c(8×2)/(4×2) surface. The higher position peak corresponds to the oxide covered surface. The 1.5 Å height difference between the oxide and clean surface is consistent with single monolayer growth consistent with the line scan analysis performed on the Fig. 4.2 STM image. Inset in Fig. 4.3(b) is expanded height distribution of In$_2$O deposited surface at the higher height region that consistent with second layer oxide growth on the oxide islands. The first and second layers of oxide have the distinct heights corresponding to distinct layers of oxide. However, the second and subsequent oxide layers appear to be amorphous since these oxides do not form ordered structures.

To form more ordered oxide structures, the effect of annealing In$_2$O/InAs(001)-c(8×2)/(4×2) was studied. Post-deposition annealing induced the oxide to spread out. As shown in Fig. 4.4, the 380°C annealed samples were more ordered with respect to both island shape and the structure within the islands consistent with the lowest energy structure being an ordered first monolayer of oxides. The ordered structures contained oxide in the troughs with rows in the [\(\bar{1}10\)] direction. Comparisons of oxide height distributions before and after annealing show the oxide height is reduced from 1.5 Å to 1.1 Å, shown in Fig. 4.5(a). For the oxide covered regions of the surface, there is a Gaussian height distribution shown in Fig. 4.5(b) with a full width at half max of only 1.8 Å which is consistent with formation of flat monolayer island structures with the 1.8 Å corrugation being primarily due to the apparent STM height difference between the
indium and oxygen atoms in In$_2$O adsorbates. Most importantly, for both room temperature deposition and post-deposition annealing, the In$_2$O adsorbates never cause the displacements of any surface atoms on the InAs(001)-c(8×2)/(4×2) surface; if the annealing temperature is raised above 450°C using cyclic annealing [29] then the In$_2$O molecules completely desorb leaving behind the clean (4×2) surface [28]. The 380°C annealing induced formation of dense flat square mono-atomically tall islands indicating that a new bonding geometry forms after post-deposition annealing. DFT simulations show that the annealed In$_2$O no longer bonds with just the As atoms at the edge of row but also forms new O-In bonds in the trough, shown in Fig. 4.4(b). For In$_2$O, In$_2$O-In trough sites are more stable than In-O-In-As edge sites by about ~0.77 eV/In$_2$O [28].

Figure 4.4. Bonding of RT deposited In$_2$O/InAs(001)-(4×2) after a 380°C anneal. (a) A filled state (Vs = -2.5 V, It = 0.2 nA, 1000 Å × 1000 Å) STM image obtained from the InAs(001)-(4×2) surface. (b) Possible atomic bonding structure diagrams of annealed In$_2$O/InAs(001)-(4×2) surface along single In$_2$O chemisorption bonding sites with top view (upper) and side view (lower).
Figure 4.5. Height analysis for RT deposition and 380°C annealing of In$_2$O/InAs(001)-(4×2). (a) Height distributions of In$_2$O deposited and annealed InAs(001)-(4×2) in Fig. 4.4(a). (b) Height distribution of only the oxide covered regions of In$_2$O deposited and annealed InAs(001)-(4×2) in Fig. 4.5(a). There are two position peaks corresponding to the clean surface region and oxide covered surface region, respectively. The distance between two peaks is 1.1 Å.
4.4.2. Silicon Monoxide (SiO)

Figure 4.6 shows a STM image of the InAs(001)-(4×2) surface after low coverage SiO deposition (~ 4% ML) at 300K with post-deposition annealing (PDA). The bright features on the surface are SiO molecules bonding with the InAs(001)-(4×2) substrate; some of the SiO bond to the rows and some of the SiO bond in the troughs. Magnified STM images show that there are three distinct types of bright features presented on the SiO/InAs(001)-(4×2) surface, which have been denoted by a hexagon, a circle and a square. These bright sites can be clearly differentiated by line scan analysis. The results show that these bright sites represent heights of three different oxide layers. The hexagon [Fig. 4.6(b)] is found to image as 1.8 Å above the surface row. This height represents monolayer height since it is close to the height of a single SiO molecule on GaAs(001)-(2×4) surface [29]. The circle [Fig. 4.6(c)] is found to image as 3.8 Å above the surface row, indicating two layer SiO molecules on surface. The square [Fig. 4.6(d)] is found to image as 5.7 Å above the surface row, indicating three layer SiO molecules on surface. These bright features are consistent with the higher self-binding energy of SiO molecules to form multilayer structures on InAs(001)-(4×2) [33].
Figure 4.6. STM image of the InAs(001)-(4×2) surface after low coverage SiO deposition (~ 4% ML) at 300 K with PDA. (a) A filled state (Vs = -2.5 V, It = 0.2 nA, 80 Å × 55 Å) STM image obtained from SiO deposited InAs(001)-(4×2) surface. Three magnified STM images illustrate three different heights with corresponding geometric symbols, and line scan corresponding to the black line on the STM image revealing that SiO adsorbates bond themselves and form nanoclusters: (b) hexagon: 1.8 Å height with 12 Å × 12 Å size, (c) circle: 3.8 Å height with 16 Å × 12 Å size, and (d) square: 5.7 Å height with 20 Å × 16 Å size. Note that a single SiO molecule’s size is about 4 Å × 4 Å according to Ref. 29.
At 35% coverage of SiO deposited on the InAs(001)-(4×2) surface at room temperature, there is no ordered oxide structure formation. SiO molecules bond to themselves and form nanoclusters shown in Fig. 4.7(a). The bonding configuration is nearly identical when the SiO/InAs sample was annealed to 380°C [Fig. 4.7(b)]. Height distribution analyses were performed on SiO deposited InAs(001)-(4×2) surface without and with PDA at 380°C. As shown in Fig. 4.7(c), for the whole surface without PDA, SiO deposited InAs(001)-(4×2) has a broad height distribution. For SiO/InAs(001)-(4×2) shown in Fig 4.7(c), there is a lower position peak (~ 7 Å height) which is the clean region of the InAs(001)-(4×2) surface. If only the oxide covered surface is included in the height distribution analysis, the results [Fig. 4.7(e)] show the SiO/InAs(001)-(4×2) surface has much broader oxide height distribution (full width at half max (FWHM) ~ 7.4 Å) which is 3.7 × as large as the height distribution for the oxide covered regions of In₂O/InAs(001)-(4×2) (FWHM ~ 2 Å) shown in Fig. 4.3. After PDA at 380°C, the height distribution becomes smoother consistent with the surface becoming slightly flatter. However, after PDA the oxide covered regions of SiO/InAs(001)-(4×2) have a FWHM of 5.9 Å which is still 3 × FWHM of the oxide covered regions for post-deposition annealed In₂O/InAs(001)-(4×2) (FWHM ~ 1.8 Å). This height distribution analysis is consistent with formation of nanoclusters for SiO deposited InAs surface. Further analysis of the SiO/InAs(001)-(4×2) surface after PDA shows no bright displaced As atoms nor dark oxygen sites. The common feature for both In₂O and SiO depositions on InAs(001)-(4×2) surface is that oxides do not displace surface atoms during both room temperature deposition and post-deposition annealing. After oxide deposition, InAs(001) surface retain the (4×2) reconstruction even within a few angstroms of the adsorbates.
Figure 4.7. STM images and the height distributions of the InAs(001)-(4×2) surface after 35% coverage of SiO deposition. Filled state (Vs = -2.5 V, It = 0.2 nA, 700 Å × 700 Å) STM images obtained from SiO deposited InAs(001)-(4×2) surface (a) without and (b) with post-deposition annealing (PDA) at 380°C. (c) Height distribution of the entire SiO/InAs(001)-(4×2) surface without PDA shown in Fig. 4.7(a). (d) Height distribution of the entire SiO/InAs(001)-(4×2) surface with PDA shown in Fig. 4.7(b). (e) Height distribution of the oxide covered regions of SiO/InAs(001)-(4×2) without PDA. (f) Height distribution of the oxide covered regions of SiO/InAs(001)-(4×2) with PDA. The green curves shown in Fig. 4.7 whole surface are the clean surface regions of SiO/InAs(001)-(4×2) surface.
The experimental results show that In$_2$O molecules completely desorb at 450 °C leaving behind the clean (4×2) surface [28], and SiO molecules remain on the surface even at 530 °C (not shown). The temperatures above 530 °C were not tried due to the heating limitations of the manipulator. Literature results show for pure substances (not InAs chemisorbates) SiO has higher sublimation energy than In$_2$O (ΔH: SiO 3.3 eV vs. In$_2$O 2.6 eV) [33]. It is hypothesized that the lower self-binding energy allows In$_2$O to form monolayer flat ordered islands, while the higher self-binding energy induces SiO to form multilayer disorder amorphous structures on InAs(001)-(4×2). Figure 4.8 shows the vapor pressure for In$_2$O and SiO versus the temperature according to experimental data of Ref. [33-35] To desorb 1 ML of In$_2$O and SiO oxide from themselves (for example: $10^{-8}$ Torr vapor pressure for 100 seconds), the oxide temperature should be 440 °C for In$_2$O and 595 °C, which is consistent with experimental results.
4.5. Conclusions

The bonding geometries of two different oxides In$_2$O and SiO on InAs(001)-c(8×2)/(4×2) were investigated using STM. The results show the completely different bonding geometries. In$_2$O molecules initially bond with As atoms at the edge of the row. After post-deposition annealing, In$_2$O molecules bond with the trough In atoms to form new O-In bonding sites. In$_2$O oxide form dense flat monolayer tall island structures on InAs(001)-c(8×2)/(4×2) surface. Conversely, SiO molecules have higher self-binding
energy so that they bond themselves and form nanoclusters on InAs(001)-c(8×2)/(4×2) surface. In$_2$O and SiO depositions on InAs(001)-c(8×2)/(4×2) surface do not displace surface atoms during both room temperature deposition and post-deposition annealing.

4.6. Acknowledgments

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Chapter 4, in full, has been accepted for publication of the material as it appears in J. Shen, W. Melitz, D. L. Feldwinn, S. Lee, R. Droopad, and A. C. Kummel, Bonding Geometries at the In$_2$O and SiO/III-V Semiconductor Interface, ECS Transaction (2010). The dissertation author was the primary investigator and author of this paper.

References


Chapter 5

Scanning Tunneling Microscopy Study of the Interfacial Bonding Structures of Ga$_2$O and In$_2$O/In$_{0.53}$Ga$_{0.47}$As(001)

5.1. Abstract

Ga$_2$O and In$_2$O oxides were deposited on In$_{0.53}$Ga$_{0.47}$As(001)-(4×2) surface by a high temperature effusion cell to investigate the interfacial bonding geometries and electronic structures by scanning tunneling microscopy/spectroscopy (STM/STS). At low coverage, Ga$_2$O molecules bond to the As atoms at the edge of the rows and preexisting Ga$_2$O on the surface. Annealing the Ga$_2$O/In$_{0.53}$Ga$_{0.47}$As(001)-(4×2) to 340 °C results in formation of slightly ordered islands running in the [-110] direction and rectangle shape flat islands on the surface. At high coverage with 340 °C post-deposition annealing (PDA), Ga$_2$O oxides form disordered structures with the large flat terraces on the surface. Conversely, at high coverage with 380 °C PDA, In$_2$O on In$_{0.53}$Ga$_{0.47}$As(001)-(4×2) forms ordered structures running in the [110] direction. STS results show that Ga$_2$O oxide does not passivate the interface nor unpin the In$_{0.53}$Ga$_{0.47}$As(001)-(4×2) surface consistent with its inability to form monolayer ordered islands on the surface; conversely, In$_2$O/ In$_{0.53}$Ga$_{0.47}$As(001)-(4×2) has an ordered monolayer coverage and is unpinned.
5.2. Introduction

The semiconductor industry has been geometrically scaling the physical dimensions of complementary metal-oxide semiconductor (CMOS) devices. Silicon based metal-oxide semiconductor field-effect transistor (MOSFET) technology is rapidly approaching its physical limits. Alternative materials may be required to continue the progress in device scaling predicted by Moore’s Law. InGaAs and related III-V compound semiconductors might provide a solution because they exhibit ~ 5-20 times higher effective channel mobility than silicon [1,2]. The key to fabricating a practical III-V MOSFET is forming an unpinned oxide/semiconductor interface with low fixed charge and low trap density [3]. Fermi level pinning can be caused by strong perturbations to the electronic structure of the oxide/semiconductor interface which induce formation of interface trap states. These perturbations can be caused by formation of localized charges, interface dipoles, or dangling bonds. In order to obtain a fundamental understanding of surface passivation of III-V compound semiconductors, it is critical to investigate and understand the oxide/semiconductor interface bonding at the atomic level.

In this study, oxide morphologies and the possible bonding geometries of two different oxides, Ga$_2$O and In$_2$O on group III rich In$_{0.53}$Ga$_{0.47}$As(001)-(4×2) along with the electronic structure of Ga$_2$O on In$_{0.53}$Ga$_{0.47}$As(001) were explored. Scanning tunneling microscopy (STM) was used to determine the interfacial bonding structure of Ga$_2$O and In$_2$O on In$_{0.53}$Ga$_{0.47}$As(001)-(4×2) after the room temperature oxide deposition and post-deposition annealing (PDA). Scanning tunneling spectroscopy (STS) measurements were performed to determine the Fermi level of the
Ga$_2$O/In$_{0.53}$Ga$_{0.47}$As(001)-(4×2) interface; the STS of the Fermi level of the In$_2$O/In$_{0.53}$Ga$_{0.47}$As(001)-(4×2) interface was also measured but previously reported [4].

5.3. Experimental Method

Molecular beam epitaxy (MBE) was employed to grow 200 nm of 1×10$^{18}$ cm$^{-3}$ doped In$_{0.53}$Ga$_{0.47}$As on 2 inch InP(001) 1×10$^{18}$ cm$^{-3}$ doped substrates (both $p$-type and $n$-type). 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. The growth rate was 0.4 ML/sec, determined by reflection high-energy electron diffraction (RHEED) intensity oscillations, at a temperature just below the transition of the (2×4) to the (4×2) surface. The wafers were capped, in situ, with a 50 nm protective As$_2$ cap. The wafers were transferred to a vacuum container for transporting to the STM chamber. The STM chamber is equipped with low energy electron diffraction (LEED), a high temperature effusion cell, and an Omicron variable temperature STM. The As capped wafers were radiatively heated to obtain the In$_{0.53}$Ga$_{0.47}$As(001)-(2×4) or (4×2) reconstruction [5]. After the (2×4) or (4×2) surface reconstruction was verified by LEED, the sample was transferred to the STM. STM images were taken at room temperature using constant-current mode. Subsequently, Ga$_2$O was deposited by evaporating sintered Ga$_2$O$_3$ from high temperature effusion cell contained in a differentially pumped chamber. Figure 5.1 shows a schematic diagram of the oxide deposition setup used in this experiment. Ga$_2$O$_3$(s) sublimates as Ga$_2$O(g) and O$_2$(g) at 1485°C [3]. However due to the low sticking probability of O$_2$ on group III-rich (4×2) surfaces [6], the majority of the adsorbing species are Ga$_2$O. An identical deposition system was used for In$_2$O.
Figure 5.1. A schematic diagram of the oxide deposition system. Ga$_2$O was deposited by evaporating sintered Ga$_2$O$_3$ (s) from a high temperature effusion cell contained in a differentially pumped chamber. Ga$_2$O$_3$ (s) sublimes as Ga$_2$O(g) and O$_2$(g) at 1485˚C [3]. However due to the low sticking probability of O$_2$ on group III-rich (4×2) surfaces, the majority of the adsorbing species are Ga$_2$O.

5.4. Results and Discussion

5.4.1. Surface Reconstruction

In$_{0.53}$Ga$_{0.47}$As(001) surface has several different reconstructions [7-9]. For our decapping and annealing method, there are three temperature regions for different surface reconstructions as shown in Table 5.1. Figure 5.2 shows 300 K STM images of clean In$_{0.53}$Ga$_{0.47}$As(001) surfaces with these three different reconstructions from three different annealing (PDA) temperatures: (a) for 330 – 400 °C annealing temperature, the surface has mainly the α2(2×4) reconstruction with small regions of β2(2×4) reconstructions; (b) for 400 – 440 °C annealing temperature, the surface has a mixture of (2×4)/(4×2) reconstructions; (c) for > 450 °C annealing temperature, nearly all regions have the (4×2) reconstruction. Since the As-rich reconstruction contains a mixture of surface reconstructions, the current study focuses on the In/Ga-rich (4×2) reconstruction. Even if a pure As-rich (2×4) reconstruction could be generated, there are additional advantages to performing experiments on the In/Ga rich (4×2) reconstruction. The (2×4) surface contains As dimers which are readily displaced by O$_2$ [10-12]; displaced As atoms are
likely to pin the Fermi level. The In/Ga rich reconstruction was chosen for oxide/InGaAs bonding structure study because it is resistant to oxidation due to the absence of As dimers on In/Ga-rich (4×2) surface[6].

Table 5.1. Annealing temperature regions for different surface reconstructions.

<table>
<thead>
<tr>
<th>Reconstruction</th>
<th>As rich (2×4)</th>
<th>Mixed (2×4) and (4×2)</th>
<th>In/Ga rich (4×2)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Annealing temperature</td>
<td>330 ~ 400 °C</td>
<td>400 ~ 440 °C</td>
<td>&gt; 450 °C</td>
</tr>
</tbody>
</table>
Figure 5.2. Filled state STM images taken at 300 K of the In$_{0.53}$Ga$_{0.47}$As(001) surface with schematic diagrams for three different reconstructions. (a) 380 °C annealed As rich InGaAs(001)-(2×4). (b) 430 °C annealed mixed (2×4) and (4×2); (2×4) and (4×2) surface regions are marked. The 2×4 regions have nearly horizontal rows running in the [-110] direction while the 4×2 regions have nearly vertical rows running in the [110] direction. (c) 460 °C annealed In/Ga rich InGaAs(001)-(4×2). (d) InGaAs(001)-α2(2×4) has As row and trough dimers and In/Ga edge dimers. (e) InGaAs(001)-β2(2×4) has row and trough As dimers. (d) InGaAs(001)-(4×2) has undimerized row and In/Ga trough dimers. Note that for (2×4) structure, STM image shows most of areas are α2(2×4), and a few of them are β2(2×4) [5].
Figure 5.3. Filled state STM images of Ga$_2$O deposited In$_{0.53}$Ga$_{0.47}$As(001)-(4×2) surface at 300 K. (a) Clean In$_{0.53}$Ga$_{0.47}$As(001)-(4×2) surface. (b) Low coverage of Ga$_2$O on In$_{0.53}$Ga$_{0.47}$As(001)-(4×2) with 110 °C PDA; the square outlines the most probable chemisorption site with an oxide height about 1.6 Å between the oxide and the rows of the clean surface, and the circle outlines a common site with an oxide height about 2.5 Å between the oxide and the rows of the clean surface. (c) Medium coverage of Ga$_2$O on In$_{0.53}$Ga$_{0.47}$As(001)-(4×2) with 340 °C PDA. (d) High coverage of Ga$_2$O on In$_{0.53}$Ga$_{0.47}$As(001)-(4×2) with 340 °C PDA. Two expanded STM images from the low coverage dose with 110 oC PDA illustrate two different heights with corresponding geometric symbols, line scan corresponding to the black line on the STM image, and possible bonding structures: (e) a Ga$_2$O molecule bonds to the As atoms at the edge of the rows and forms new Ga-As bonds; 1.6 Å oxide height, and (f) a Ga$_2$O molecule bonds with a preexisting Ga$_2$O on the surface and forms new Ga-O bonds; 2.5 Å oxide height.
(a) Clean Surface

(b) Low Coverage

(c) Medium Coverage

(d) High Coverage

(e) 1.6 Å

(f) 2.5 Å
5.4.2. Ga$_2$O/In$_{0.53}$Ga$_{0.47}$As Bonding

Ga$_2$O was deposited on the surface to determine the oxide bonding structure on the In$_{0.53}$Ga$_{0.47}$As(001)-(4×2) surface. When Ga$_2$O$_3$(s) is evaporated from a high temperature effusion cell, it forms Ga$_2$O(g) and O$_2$(g) at 1485 °C [3]. The O$_2$(g) does not stick on the room temperature In$_{0.53}$Ga$_{0.47}$As(001)-(4×2) clean surface so In$_{0.53}$Ga$_{0.47}$As is covered with Ga$_2$O(s). Deposition at room temperature results in a nearly amorphous structure. At low coverage, the most probable chemisorption sites are Ga$_2$O molecules bonding to the As atoms at the edge of the rows with an oxide height of about 1.6 Å between the oxide and the rows of the clean surface shown in Fig. 5.3(e); in addition, the Ga$_2$O molecules bonding with preexisting Ga$_2$O on the surface have an oxide height of about 2.5 Å between the oxide and the rows of the clean surface shown in Fig. 5.3(f). At medium coverage, a 340 °C PDA results in formation of slightly ordered islands running in the [-1-10] direction; rectangle shape flat islands are observed with an oxide height of 1–1.2 Å. At high coverage with 340 °C PDA, Ga$_2$O oxides form disordered structures with the large flat terraces on the surface. While the height of the high coverage oxide islands with 340 °C PDA cannot be directly determined since the surface is completely covered with oxide, the step edge height of Ga$_2$O deposited In$_{0.53}$Ga$_{0.47}$As(001)-(4×2) is the same as on clean In$_{0.53}$Ga$_{0.47}$As(001)-(4×2) surface ( ~ 2.8 Å ) consistent with the theoretical step edge value for In$_{0.53}$Ga$_{0.47}$As(001) surface (half lattice constant, 2.93 Å). RMS roughness for the high coverage of Ga$_2$O deposited In$_{0.53}$Ga$_{0.47}$As(001)-(4×2) is about 1.2 Å. The ~ 2.8 Å step edge height and the low RMS roughness are consistent with the 340 °C PDA high coverage islands having the same structure and height (1–1.2 Å) as the 340 °C PDA medium coverage islands. The bonding structure of the annealed
Ga$_2$O deposited on In$_{0.53}$Ga$_{0.47}$As(001)-(4×2) looks different than the bonding structure of In$_2$O deposited on In$_{0.53}$Ga$_{0.47}$As(001)-(4×2).

5.4.3. In$_2$O/In$_{0.53}$Ga$_{0.47}$As Bonding

When In$_2$O$_3$(s) is evaporated from a high temperature effusion cell, it forms In$_2$O(g) and O$_2$(g) at 1000 – 1025 °C [13]. Similar to Ga$_2$O deposition, the O$_2$(g) does not stick on the room temperature In$_{0.53}$Ga$_{0.47}$As(001)-(4×2) clean surface so In$_{0.53}$Ga$_{0.47}$As is covered with In$_2$O(s). A filled-state STM image shown in Fig. 5.4(a) reveals that at low coverage, In$_2$O molecules mainly occupy single sites at the edge of the rows [4]. The In$_2$O most likely form new In-As bonds to the surface. Fig. 5.4(d) shows the expanded STM image from Fig. 5.4(a) with corresponding hexagon symbol, line scan corresponding to the black line on the STM image, and possible bonding structure. At medium coverage with 380 °C PDA, an ordered oxide surface structure was observed. Comparisons of oxide height difference before and after annealing show that the height difference between deposited In$_2$O oxide and surface rows is reduced from 1.5 Å to 1-1.2 Å. It is likely that the annealed In$_2$O molecules no longer bond with the row edge As atoms but also form new O-In/Ga bonds in the trough thereby reducing the oxide height difference as confirmed by density function theory (DFT) calculations [4]. For the full coverage with 380 °C PDA, the In$_2$O oxide forms ordered structures running in the [110] direction on In$_{0.53}$Ga$_{0.47}$As(001)-(4×2) surface, which is completely different to that of Ga$_2$O deposited on In$_{0.53}$Ga$_{0.47}$As(001)-(4×2). It is noted that there is substantial amount of second layer growth with 0.9 Å RMS roughness probably due to In$_2$O-In$_2$O
interactions, but these are sufficiently weak to allow full coverage formation of an In$_2$O overlayer.

Figure 5.4. In$_2$O deposited In$_{0.53}$Ga$_{0.47}$As(001)-(4×2) surface. (a) Low coverage of In$_2$O on In$_{0.53}$Ga$_{0.47}$As(001)-(4×2). (b) Medium coverage of In$_2$O on In$_{0.53}$Ga$_{0.47}$As (001)-(4×2) with 380 °C PDA. The first layer sites are yellow (red arrow), while the second layer sites are white (blue arrow). (c) High coverage of In$_2$O on In$_{0.53}$Ga$_{0.47}$As(001)-(4×2) with 380 °C PDA. The first layer sites are yellow (red arrow), while the second layer sites are white (blue arrow). (d) Expanded STM image from Fig. 5.4(a) with corresponding hexagon symbol, line scan corresponding to the black line on the STM image, and possible bonding structure.
A possible reason for the lack of order for Ga$_2$O/In$_{0.53}$Ga$_{0.47}$As(001)-(4×2) is the Ga$_2$O molecules forming strong bonds to In$_{0.53}$Ga$_{0.47}$As(001)-(4×2) as well as strong oxide-oxide bonds thereby inhibiting diffusion. DFT calculations have been performed for Ga$_2$O and In$_2$O on As-rich InGaAs(001)-(2×4) showing that the bonding energies are -1.86 eV/Ga$_2$O and -1.12 eV/In$_2$O for the row insertion sites [14]; while the bonding sites are different on In/Ga-rich InGaAs(001)-(4×2) a similar difference in bonding energies is expected for Ga$_2$O and In$_2$O on InGaAs(001)-(4×2) since Ga-As bonds are stronger than In-As bonds consistent with the lower diffusion of Ga$_2$O than that of In$_2$O on InGaAs(001)-(4×2).

5.4.4. Electronic Structure

Scanning tunneling spectroscopy (STS) was used to measure the electronic structure of the surface. The STS of the clean surface shows the Fermi level pinning (see blue curves shown in Fig. 5.5). Both the clean $n$-type and $p$-type samples have a Fermi level (0 V position in STS) at the valance band edge. The Fermi level shift for $n$-type sample may be caused by surface band bending or by gap states. A surface dipole may exist since In$_{0.53}$Ga$_{0.47}$As(001)-(4×2) has a high density of defects which might induce a surface dipole [9]. After Ga$_2$O deposition and annealing, the STS spectra does not change as shown in by green curves; this is consistent with Ga$_2$O not electronically passivating the interface and Ga$_2$O/In$_{0.53}$Ga$_{0.47}$As(001)-(4×2) surface being pinned. For In$_2$O/In$_{0.53}$Ga$_{0.47}$As(001)-(4×2), the Fermi level position is close to the conduction band minimum (CBM) for $n$-type samples while close to the valence band maximum (VBM) for $p$-type samples, which is consistent with an unpinned surface. The detailed STS
results of In$_2$O/In$_{0.53}$Ga$_{0.47}$As are discussed elsewhere [4]. It is possible that the low diffusivity of Ga$_2$O on the high defect density In$_{0.53}$Ga$_{0.47}$As(001)-(4×2) surface prevents formation of oxide islands with sufficient order and coverage to remove the surface dipole and create an unpinned surface. Ga$_2$O deposited on GaAs(001)-(2×4) is a good example for unpinning. Hale et al. have reported STM/STS results of Ga$_2$O deposited on GaAs(001)-(2×4) [3]. STS results show for Ga$_2$O deposited on \textit{n}-type GaAs(001)-(2×4) samples, the Fermi level position is close to CBM consistent with unpinning in contrast with Ga$_2$O deposited on \textit{n}-type InGaAs(001)-(4×2). STM results show Ga$_2$O oxide forms monolayer ordered structure on GaAs(001)-(2×4) in which the Ga$_2$O inserts into As-As bonds to restore the surface to bulk-like termination. Since there are no As-As dimers on the InGaAs(001)-(4×2) surface, the Ga$_2$O As dimer insertion sites cannot exist on InGaAs(001)-(4×2) consistent with Ga$_2$O/InGaAs(100) being both unable to form monolayer order structures and with the surface being pinned.
Figure 5.5. Scanning tunneling spectra for the In$_{0.53}$Ga$_{0.47}$As(001)-(4×2) clean surface and Ga$_2$O deposited In$_{0.53}$Ga$_{0.47}$As(001)-(4×2) surface: (a) p-type sample; (b) n-type sample. For both p-type and n-type In$_{0.53}$Ga$_{0.47}$As(001)-(4×2) clean surfaces, the Fermi level (0 V) lies near the valence band maximum (VBM). After Ga$_2$O oxide deposition, for both p-type sample and n-type samples, the Fermi level still remain near VBM. These results indicate that the Fermi level is still pinned after Ga$_2$O deposition.

5.5. Conclusions

The bonding geometries of two different oxides Ga$_2$O and In$_2$O on In$_{0.53}$Ga$_{0.47}$As(001)-(4×2) were investigated using STM. The results show at low coverage, both Ga$_2$O and In$_2$O molecules bond to the As atoms at the edge of the rows. However, Ga$_2$O molecules also bond to preexisting Ga$_2$O oxide on the surface. At high full coverage with post-deposition annealing, Ga$_2$O oxide forms disordered structures with the large flat terraces on the surface, while In$_2$O oxide forms ordered structures running in the [110] direction on In$_{0.53}$Ga$_{0.47}$As(001)-(4×2). STS results show that Ga$_2$O oxide does not passivate the interface nor unpin the In$_{0.53}$Ga$_{0.47}$As(001)-(4×2) surface consistent with its inability to form monolayer ordered islands on the surface.
5.6. Acknowledgements

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References:


Chapter 6

Scanning Tunneling Microscopy/Spectroscopy Study of Atomic and Electronic Structures of In$_2$O on InAs and In$_{0.53}$Ga$_{0.47}$As(001)-(4×2)

6.1. Abstract

Interfacial bonding geometry and electronic structures of In$_2$O on InAs and In$_{0.53}$Ga$_{0.47}$As(001)-(4×2) have been investigated by scanning tunneling microscopy/spectroscopy (STM/STS). STM images show that the In$_2$O forms an ordered monolayer on both InAs and InGaAs surfaces. In$_2$O deposition on the InAs(001)-(4×2) surface does not displace any surface atoms during both room temperature deposition and post-deposition annealing. Oxygen atoms from In$_2$O 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 bulk-like tetrahedral sp$^3$ bonding environments. Scanning tunneling spectroscopy (STS) reveals that for both $p$-type and $n$-type clean In$_{0.53}$Ga$_{0.47}$As(001)-(4×2) surfaces, the Fermi level resides near the valence band maximum (VBM); however, after In$_2$O deposition and post-deposition annealing, the Fermi level position is close to the VBM for $p$-type samples and close to the conduction band minimum (CBM) for $n$-type samples. This result indicates that In$_2$O bonding eliminates surface states within the band gap and forms an unpinned interface when bonding with In$_{0.53}$Ga$_{0.47}$As/InP(001)-(4×2). Density function theory (DFT) is used to confirm the experimental finding.
6.2. 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 (~ 4×10⁴ cm² V⁻¹s⁻¹ and 1×10⁴ cm² V⁻¹s⁻¹) compared to Si (~1.5×10³ cm² V⁻¹s⁻¹) at 300 K [5,6]. A few InAs based FETs [2,7] and many InGaAs based MOSFETs [8-11] structures have previously demonstrated potential for high performance III-V MOSFET devices. Although InAs(001) [12-14] has been the focus of many scanning tunneling microscopy (STM) studies, very few STM studies have been performed on In₀.₅₃Ga₀.₄₇As(001) [15,16]. Furthermore, only one STM study has been performed on atomic bonding geometry of
oxide/InAs or InGaAs(001) interfaces. The current paper focuses on the oxide bonding to the group III-rich (4×2) reconstruction of InAs and InGaAs(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 O_2 during oxide deposition thereby pinning the Fermi level directly or indirectly [17-20]. Conversely, the group III-rich reconstructions are less reactive to O_2 and, therefore, are probably quite suitable for oxide deposition [21].

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. Scanning tunneling microscopy (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 temperature oxide deposition. In addition, the effects of post-deposition annealing on In_2O 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)-(4×2) interfaces to investigate the electronic structures and determine the Fermi level pinning for this surface since the band gap 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 been determined.

6.3. 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*. MBE is employed to grow 0.2 micron of either \(1 \times 10^{18} \text{ cm}^{-3}\) doped InAs on InAs(001) \(1 \times 10^{18} \text{ cm}^{-3}\) doped substrates, or \(1 \times 10^{18} \text{ cm}^{-3}\) doped \(\text{In}_{0.53}\text{Ga}_{0.47}\text{As}\) on lattice-matched \(\text{InP}(001) \ 1 \times 10^{18} \text{ cm}^{-3}\) doped substrates. Both \(p\)-type and \(n\)-type samples are grown and capped *in situ* with 500 Å of As\(_2\) 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 preparing chamber [14,22]. 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. The clean (4×2) surfaces can be observed with both filled and empty state STM imaging. Subsequently, indium oxide is deposited by evaporating sintered \(\text{In}_2\text{O}_3(s)\) (Aldrich Chem. Co.) from a high temperature effusion cell (Applied EPI) contained in a differentially pumped chamber. \(\text{In}_2\text{O}_3(s)\) sublimes as \(\text{In}_2\text{O (g) and O}_2 (g)\) at 1000-1025 °C [23]. However, due to the low sticking probability of \(\text{O}_2\) on group III-rich (4×2) surfaces [21], the majority of the adsorbing species are \(\text{In}_2\text{O}\).

All DFT simulations are performed with the Vienna Ab-initio Simulation Package (VASP) [24,25] using projector augmented-wave (PAW) pseudopotentials (PP) [26,27] and PBE (Perdew-Burke-Ernzerhof) exchange-correlation functional [28,29]. 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 4×4×1 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 7 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. [30]. The slabs are relaxed using Conjugate-Gradient (CG) 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 (PBC). To compensate for the spurious electric field induced by PBC for this type of system, a dipole correction is applied [24,25,31]. 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 [14,22].
Figure 6.1. Dual state STM images of InAs(001)-(4×2) with atomic structure model. (a) A filled state ($V_s = -1.6$ V, $I_t = 0.2$ nA, 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, 100 Å × 100 Å) STM images of InAs(001)-(4×2) clean surface. (c) An undimerized atomic structure model [14] for InAs(001)-(4×2) reconstruction based on which was originally proposed in Ref. [12] and Ref. [13]. The green rectangle presents a unit cell of (4×2). Note that the empty state image is taken in Park Scientific RT-STM system, and In atoms on the row are undimerized, and same height with As atoms at the edge of row.
6.4. Experimental Results

6.4.1. InAs(001)-(4×2) Surface

Figure 6.1 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 17Å. These In rows have dicoordinated sp hybridized In atoms forming π bonds with tricoordinated As atoms at the edge of the row [14,22]. 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. 6.1(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, In$_2$O molecules are deposited onto the room temperature InAs clean surface to study the oxide bonding. STM images of In$_2$O/InAs(001)-(4×2) surface are shown in Fig. 6.2 along with a structural model illustrating the possible oxide bonding structure for room temperature deposition. In filled state STM images, In$_2$O is imaged as a bright feature on the clean InAs(001)-(4×2) surface. According to STM observations, nearly all the bonding sites are consistent with In$_2$O bonding to the clean InAs(001)-(4×2) surface since O$_2$ chemisorption sites on the InAs(001)-(4×2) surface appear as dark cuts in the top In rows [21]. A high resolution scan of a small region of the room temperature low coverage In$_2$O/InAs(001) surfaces reveals that the In$_2$O molecules only occupy single sites at the edge of the rows. These In$_2$O adsorbates most likely form new In-As bonds on the surface. The line scan profile in Fig. 6.2(d) along [1 1 0] direction shows the distance between the two bright In$_2$O sites is about 8.5 Å which is identical to the repeat distance
of the possible bonding sites proposed in Fig. 6.2(c). Note, 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 6.2(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 [4,19].

Figure 6.2 STM images and structure model with line scan of In$_2$O deposited on InAs(001)-(4×2) surface. (a) A filled state ($V_s = -1.5$ V, $I_t = 0.2$ nA, 520 Å × 520 Å) STM image of the InAs(001)-(4×2) surface with ~25% coverage of In$_2$O. (b) Expanded STM image taken from the green box in Fig. 6.2(a). (c) An atomic bonding structure model for In$_2$O deposition on InAs(001)-(4×2) surface. (d) Line scanning profiles and atomic bonding structure diagrams of In$_2$O/InAs(001)-(4×2) surface along single In$_2$O chemisorption bonding sites perpendicular [-1 1 0] (top) and parallel [1 1 0] (bottom) directions, respectively. Note that this image is taken in Park Scientific RT-STM system.
Figure 6.3. STM images of medium coverage In$_2$O deposited on InAs(001)-(4×2) surface with two different post-deposition annealing. Filled state ($V_s = -1.5$ V, $I_t = 0.2$ nA, 450 Å × 450 Å) STM images of sub-monolayer In$_2$O deposited InAs(001)-(4×2) surface after post-deposition annealing at (a) 390 °C and (b) 450 °C. After 390 °C post-deposition annealing, the oxide is spread out, and the coverage increases from ~ 25% to ~ 45%. After 450 °C post-position annealing, all of the oxide is desorbed from InAs surface and leaving behind a clean (4×2) surface. Note Fig. 6.3(b) image is not taken from original clean InAs(001)-(4×2) surface, and it is taken from oxide deposited surface after high temperature post-deposition annealing.
At medium coverage (25% of a monolayer), the In$_2$O adsorbates form islands that are elongated in the [1 1 0] direction as shown in Fig. 6.2(a). Prior to all the first layer sites being occupied with In$_2$O 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 [32]. 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. 6.2(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 [32]. 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$_2$O/InAs(001)-(4×2) is studied. After post-deposition annealing, the oxide spreads out. As shown in Fig. 6.3(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 [-1 1 0] direction. The distance between the ordered oxide row is 8.5-13 Å in the [1 1 0] direction, which is close to 2-3× the span of the InAs(001) bulk unit cell (4.3 Å). Comparisons of oxide height distributions before and after annealing show the oxide height is reduced from 1.5 Å to 1 Å. Most importantly, for both room temperature deposition and post-deposition annealing, the In$_2$O 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 [33], the In$_2$O molecules completely desorb leaving behind the clean (4×2) surface, as shown in Fig. 6.3(b). The observations of ordered monolayer In$_2$O islands and desorption at around 450 °C is consistent with the In$_2$O 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$_2$O/InAs(001)-(4×2) after post-deposition annealing at 380 °C, the oxide form large, well-ordered, flat terraces on the surface, as shown in Fig. 6.4. 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. 6.4(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 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 sub-monolayer 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 [22], and the stronger bonding of the oxide to InAs(001)-(4×2) than the oxide to itself facilitate surface oxide molecular diffusion to assist in the formation of an ordered flat first oxide layer.
Figure 6.4. STM images of high coverage In$_2$O deposited on InAs(001)-(4×2) surface with post-deposition annealing. (a) A filled state ($V_s = -3$ V, $I_t = 0.15$ nA, 1000 Å × 1000 Å) STM image of the InAs(001)-(4×2) surface with almost 1 ML coverage of In$_2$O after post-deposition annealing at 380 °C. (b) Expanded STM image (250 Å × 250 Å) taken from the green box in Fig. 6.4(a). A small unreacted portion of the (4×2) clean surface is labeled as “A” in the STM image.
Figure 6.5. A filled state ($V_s = -3$ V, $I_t = 0.15$ nA, 600 Å × 600 Å) STM image of the In$_{0.53}$Ga$_{0.47}$As(001)-(4×2) clean surface.

6.4.2. 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$_2$O/InAs(001)-(4×2) 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 facilitates the electronic structure determination. Shen et al. have reported STM results on the group III-rich InAs(001)-(4×2) and In$_{0.53}$Ga$_{0.47}$As(001)-(4×2) reconstructions [22]. They found that the In$_{0.53}$Ga$_{0.47}$As(001)-(4×2) and InAs(001)-(4×2) have similar STM images and, therefore, similar surface reconstructions. Fig. 6.5 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.
Figure 6.6. STM images and structure model with of In$_2$O deposited on In$_{0.53}$Ga$_{0.47}$As(001)-(4×2) surface. (a) A filled state ($V_s = -2.2$ V, $I_t = 0.2$ nA, 260 Å × 260 Å) STM image of the In$_{0.53}$Ga$_{0.47}$As(001)-(4×2) surface with low coverage of In$_2$O from room temperature deposition without annealing; the dark arrows show In$_2$O bonding sites for the first oxide monolayer growth. (b) A filled state ($V_s = -2.5$ V, $I_t = 0.2$ nA, 260 Å × 400 Å) STM images of the In$_{0.53}$Ga$_{0.47}$As(001)-(4×2) surface with a medium coverage of In$_2$O after post-deposition annealing 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 In$_2$O molecules bonding with preexisting first layer In$_2$O in the trough. (c) An empirical atomic bonding structure model for In$_2$O deposition on In$_{0.53}$Ga$_{0.47}$As(001)-(4×2) surface with top view and side view.
A filled-state STM image of low coverage In$_2$O without annealing on In$_{0.53}$Ga$_{0.47}$As(001)-(4×2) is shown in Fig. 6.6(a). STM result reveals that the low coverage In$_2$O molecules mainly occupy single sites at the edge of the rows. Similar to In$_2$O/InAs(001)-(4×2), the In$_2$O molecules on In$_{0.53}$Ga$_{0.47}$As(001)-(4×2) most likely form new In-As bonds to the surface. Figure 6.6(b) shows a STM image of medium coverage In$_2$O on In$_{0.53}$Ga$_{0.47}$As(001)-(4×2) with post-deposition annealing at 380 °C. There are two types of bright features observed with STM. The intermediate bright feature (dark arrows) shows that the In$_2$O molecules fill the trough region between the group III In/Ga rows and form ordered structures along the rows in the [1 1 0] direction, which is different than on InAs(001)-(4×2) surface. The trough In$_2$O molecules are tightly packed with few missing sites. These long range ordered structures in the [1 1 0] direction may form preferentially on In$_{0.53}$Ga$_{0.47}$As(001)-(4×2) compared to InAs(001)-(4×2) due to the greater trough defect density on the clean In$_{0.53}$Ga$_{0.47}$As(001)-(4×2) 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)-(4×2) surface than on the InAs(001)-(4×2) surface since a higher percentage of In$_2$O molecules bond with the first layer In$_2$O; these second layer In$_2$O are the brighter features indicated by green arrows in Fig. 6.6(b); this is consistent with some In$_2$O molecules bonding to defect sites thereby perturbing their electronic structure.
Figure 6.7. STM images of high coverage In$_2$O deposited on In$_{0.53}$Ga$_{0.47}$As(001)-(4×2) surface with post-deposition annealing. (a) A filled state ($V_s = -2.5$ V, $I_t = 0.25$ nA, 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 In$_2$O after post annealing at 380 °C. (b) Expanded STM image (350 Å × 350 Å) taken from the green box in Fig. 6.8(a).
The bonding configuration is different when the In$_2$O/InGaAs sample is annealed. Similar to In$_2$O/InAs case, after post-deposition annealing, the height difference between deposited oxide and surface In/Ga row is reduced from 1.5 Å to 1 Å. As shown in the DFT studies below, it is likely that the annealed In$_2$O 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 6.6(c) illustrates a possible bonding model of In$_2$O on In$_{0.53}$Ga$_{0.47}$As(001)-(4×2) surface. Note this is an empirical bonding structure, and an exact bonding structure is calculated using DFT as shown below. For full coverage of In$_2$O/In$_{0.53}$Ga$_{0.47}$As(001)-(4×2) after post-deposition annealing at 380 °C, a filled state STM image is seen in Fig. 6.7, as well as an enlarged region. From this image, it is clear that the In$_2$O forms smooth ordered structure on In$_{0.53}$Ga$_{0.47}$As surface with an RMS roughness 0.9 Å, similar to full coverage of In$_2$O on InAs(001)-(4×2).

The electronic structure of the surface has been obtained by scanning tunneling spectroscopy (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. 6.8(a) and 6.8(b), blue curves show the STS spectra of the clean $p$-type and $n$-type In$_{0.53}$Ga$_{0.47}$As(001)-(4×2) 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 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 the surface pinning is due to the strained unbuckled dimers in the trough of the 4×2 reconstruction. In Figs 6.8(a) and 6.8(b), green curves show the STS spectra after full coverage In$_2$O deposition on p-type and n-type In$_{0.53}$Ga$_{0.47}$As(001)-(4×2) surfaces with post-deposition annealing at 380 °C. The STS spectra results show that after oxide deposition and post-deposition 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 [34]. The results prove that the deposition and 380 °C annealing of In$_2$O on In$_{0.53}$Ga$_{0.47}$As(001)-(4×2) unpin interface because the Fermi level moves from the VBM towards 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 In$_2$O passivates the interface and InGaAs surface is unpinned.
Figure 6.8. Scanning tunneling spectra for the In$_{0.53}$Ga$_{0.47}$As(001)-(4×2) clean surface and monolayer coverage of In$_2$O. (a) $p$-type sample; (b) $n$-type sample. For both $p$-type and $n$-type In$_{0.53}$Ga$_{0.47}$As(001)-(4×2) clean surfaces, the Fermi level (0 V) lies near the valence band maximum (VBM). After oxide deposition and post annealing, for $p$-type sample the Fermi level remain near VBM (annealed at 380 °C), for $n$-type sample the Fermi level shifts to conduction band minimum (CBM) (annealed at 380 °C). These results indicate that the Fermi level is unpinned after In$_2$O deposition. A 50 mV amplitude and 1.5 kHz sinusoidal modulation voltage is superimposed on the tip bias, and the dI/dV spectra is recorded using a DSP lock-in amplifier (Signal Recovery 7280).
6.5. Density Function Theory Results

6.5.1. Bonding Structure

Based on experimental results, there are two potential simplified empirical bonding structures for In$_2$O on InAs and InGaAs surfaces: In-O-In-As site at the edge of row for low coverage without post-deposition annealing shown in Fig. 6.2(c), and In$_2$O-In/Ga site in the trough for intermediate or high coverage with post-deposition annealing shown in Fig. 6.6(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 In-As edge site is less stable than O-In/Ga trough site by about ~0.81 eV/In$_2$O for InGaAs surface, and ~0.77 eV/In$_2$O for InAs surface. Therefore, it is more energetically favorable for O atoms from In$_2$O molecules to bond over a trough dimer rather than just single In atoms from In$_2$O 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 post-deposition annealing because there is a kinetic barrier to In$_2$O-In/Ga bonding site formation. Calculations were performed for different oxide coverage to study the influence of In$_2$O coverage, including comparison between In$_2$O-In and In$_2$O-Ga bonding sites because experiments show the In$_2$O spontaneous forms monolayer islands while most adsorbates show repulsion or 3D cluster formation. In Fig. 6.9(a)-(c), In$_2$O-In bonding configurations and total energy differences relative to clean surface for single, double and quadruple In$_2$O molecules on double InGaAs-(4×2) unit cells are shown. The chemisorption binding energies for all In$_2$O sites on InGaAs(001)-(4×2) were calculated using the lowest energy clean surface
structure since the In$_2$O/InGaAs(001)-(4×2) 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$_2$O/InGaAs(001)-(4×2), the In$_2$O-In
chemisorption binding energies are nearly coverage independent consistent with the
absence of absorbate-absorbate repulsion. Fig. 6.9(d)-(f) shows the In$_2$O-Ga bonding
configuration with single, double and quadruple In$_2$O molecules on double InGaAs-(4×2)
unit cells. The In$_2$O-Ga chemisorption binding energies are also nearly coverage
independent consistent with the absence of absorbate-absorbate repulsion. The results
show that the In$_2$O-Ga bonding site is slightly more stable (0.2-0.3 eV/In$_2$O) than the
In$_2$O-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. In$_2$O on InAs(001)-(4×2) with single, double and quadruple In$_2$O sites are shown
in Fig. 6.9(g)-(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$_2$O site on the InAs double unit cells case [Fig.
6.9(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 [Fig.
6.9(h) and Fig 6.9(i)] are nearly identical to the In$_2$O/InGaAs(001)-(4×2) 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 In$_2$O islands on group III-rich InAs surfaces. It is noted that the DFT show
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.

Figure 6.9. DFT relaxed atomic structures for group III-rich In\textsubscript{0.5}Ga\textsubscript{0.5}As(001) and InAs reconstructions with the DFT calculated total energy differences relative to the lowest total energy clean surface case (undimerized-buckled). Note that all of InGaAs cases use the same substrate reference state. The InAs cases use two different substrate reference states since the single In\textsubscript{2}O/InAs(001) [Fig. 6.9(g)] has a different substrate structure compared the double [Fig. 6.9(h)] and quadruple [Fig. 6.9(i)] In\textsubscript{2}O/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.
6.5.2. Electronic Structure

Figure 6.10(a)-(d) show the electronic structures of full coverage In$_2$O on InGaAs(001)-(4×2). 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/In$_2$O binding energy difference range for the In$_2$O bonding on InGaAs surface. As previously discussed, most of the slight energy difference is due to differences in In$_2$O-Ga vs. In$_2$O-In bonding. Figure 6.10 also shows the density of states (DOS) of corresponding In$_2$O/InGaAs bonding structures. The DOS for two mixed In$_2$O-In/In$_2$O-Ga bonding sites is unpinned since the band gap is free of electronic states. For the In$_2$O-In only and In$_2$O-Ga only bonding sites, there are some band gap states. Two clean InGaAs(001)-(4×2) surface structures are shown in Fig. 6.10(e)-(f) along with their DFT calculated electronic structures. The group III dimers in the trough cause a large buckling in the lowest energy structure which relieves stress [Fig. 6.10(f)], 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 6.8 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 6.10(e)]. The STM/STS data and the DFT modeling is 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 Fig 6.10(a)-(e), at full coverage, In$_2$O bonding restores about half the trough group III atoms to four-coordinate sp$^3$ hybridized bonding.
thereby eliminating the strain for these trough sites. For the mixed In$_2$O-In/In$_2$O-Ga bonding geometry, the DFT shows that the reduction in strain is sufficient to eliminate the midgap states. The mixed In$_2$O-In/In$_2$O-Ga bonding geometry resembles more closely to the experimental results because deposited oxide doesn’t form completed ordered structures on the group III-rich InGaAs(001) surface and the group III-rich surface contains a mixture of In and Ga atoms.
Figure 6.10. DFT bonding structures of In$_2$O/In$_{0.5}$Ga$_{0.5}$As(001) and calculated density of states. (a)-(d) O-In, mixed O-In/Ga or O-Ga bonding structure with four In$_2$O 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.
6.5.3. Oxides on GaAs, InAs and InGaAs Comparison

The bonding of $\text{In}_2\text{O}$ on group III-rich InGaAs(001)-(4×2) is quite distinct from the bonding of $\text{O}_2$, $\text{In}_2\text{O}$ and $\text{Ga}_2\text{O}$ on the As-rich GaAs(001)-(2×4) surfaces[4,19,23]. For $\text{O}_2$ 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, $\text{Ga}_2\text{O}$ molecules preferentially bond to As dimer rows and form Ga-As bonds. At monolayer $\text{Ga}_2\text{O}$ coverage, the GaAs(001)-(2×4) surface undergoes a surface reconstruction resulting in (2×2) surface periodicity, which has completed As termination with $\text{Ga}_2\text{O}$ molecules inserted in As dimer pairs on the row. This new surface and bonding restore near bulk-like surface charges and unpins the surface after $\text{Ga}_2\text{O}$ deposition. For the $\text{In}_2\text{O}$ on the GaAs(001)-(2×4) surface, the As-As insertion site is not favorable for initial $\text{In}_2\text{O}$ bonding. $\text{In}_2\text{O}$ initially bonds in the trough regions forming stable In-O-In-Ga bonds. At higher coverage with post-deposition annealing, $\text{In}_2\text{O}$ molecules start to insert in or between As dimers pairs on the row and bond with preexisting first layer $\text{In}_2\text{O}$ 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 $\text{In}_2\text{O}/\text{GaAs}(001)$-(2×4) being pinned.

$\text{In}_2\text{O}$ chemisorption on $\text{In}_{0.53}\text{Ga}_{0.47}\text{As}(001)$-(4×2) is completely different. $\text{In}_2\text{O}$ molecules initially bond to As atoms at the edge of row and form In-O-In-As bonds. At high coverage with post-deposition annealing, $\text{In}_2\text{O}$ molecules fill the trough region, bond together, and form long range ordered structure along the row in the [1 1 0] direction. These new $\text{In}_2\text{O}$-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 In$_2$O 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 bulk-like tetrahedral sp$^3$ bonding geometry and unpins the In$_{0.53}$Ga$_{0.47}$As(001)-(4×2) surface.

### 6.6. Conclusions

STM/STS is used to determine the atomic bonding geometry and electronic structures of In$_2$O adsorbed group III-rich InAs and In$_{0.53}$Ga$_{0.47}$As(001)-(4×2) surface. STM results show that without annealing, In atoms from In$_2$O bond with substrate As atoms at the edge of row to form In-O-In-As bonds. With post-deposition annealing In$_2$O overcomes kinetic barriers and O atoms from In$_2$O bond with In/Ga atoms in the trough to form new In$_2$O-In/Ga bonds which restores trough In/Ga atoms into a more bulk-like tetrahedral sp$^3$ bonding environment and releases the strain. This bonding is sufficiently favorable since In$_2$O-In/Ga trough sites are more stable than In-O-In-As edge sites by about $\sim$0.81 eV/In$_2$O for InGaAs surfaces and $\sim$0.77 eV/In$_2$O for InAs surfaces. High temperature post-deposition annealing results show an ordered In$_2$O monolayer with weak bonding since the layer can readily be desorbed without displacing surface atoms. STS spectra results clearly show In$_2$O deposited In$_{0.53}$Ga$_{0.47}$As(001)-(4×2) surface has an unpinned interface after post-deposition 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 band gap. Although the process window is narrow, the result proves that oxide bonding
can unpinned a pinned III-V semiconductor surface, and the results provide a bonding model for this process.

6.7. Acknowledgements

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