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UNIVERSITY OF CALIFORNIA, SAN DIEGO

PROPERTIES OF ADSORBATES
ON III-V SEMICONDUCTORS

A dissertation submitted in partial satisfaction of the
requirements for the degree Doctor of Philosophy
in
Chemistry
by
Darby L. Winn

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2007
The dissertation of Darby L. Winn is approved, and it is acceptable in quality and form for publication on microfilm:


Chair

UNIVERSITY OF CALIFORNIA, SAN DIEGO

2007
DEDICATION

This thesis is dedicated to my Dad (Will Winn), Mom (Nancy Winn) and Alex Feldman without whose support this would never have been possible.
# TABLE OF CONTENTS

Signature Page .......................................................................................................................... iii  
Dedication ................................................................................................................................ iv  
Table of Contents ..................................................................................................................... v  
List of Symbols and Abbreviations ......................................................................................... viii  
List of Figures ......................................................................................................................... x  
List of Tables .......................................................................................................................... xiii  
Preface ....................................................................................................................................... xiv  
Acknowledgements ................................................................................................................. xvii  
Vita ............................................................................................................................................ xix  
Abstract of the Dissertation ................................................................................................. xxii  

**Chapter One** Direct and Indirect Causes of Fermi Level Pinning at the SiO/GaAs Interface........ 1  
1.1 Abstract ............................................................................................................................ 1  
1.2 Introduction ...................................................................................................................... 2  
1.3 Experimental Techniques ............................................................................................... 3  
1.4 Experimental Results and Discussion .......................................................................... 4  
1.5 Computational Results and Discussion ....................................................................... 14  
1.6 Conclusion ....................................................................................................................... 27  
1.7 Figures ............................................................................................................................ 28  
1.8 Tables ............................................................................................................................ 41
1.9 Acknowledgments .................................................................................................. 43

**Chapter Two** Electronic Properties of Adsorbates on GaAs(001)-(2×8)/(2×4) ...................... 44

2.1 Abstract ................................................................................................................. 44
2.2 Introduction .......................................................................................................... 45
2.3 Experimental and Computational Techniques ...................................................... 46
2.4 Results and Discussion ....................................................................................... 47
2.5 Conclusion .......................................................................................................... 62
2.6 Figures ................................................................................................................. 64
2.7 Acknowledgments ............................................................................................. 73

**Chapter Three** Definitive Identification of the InAs(001)-(8×2)/(4×2) Reconstruction .............. 74

3.1 Abstract ................................................................................................................. 74
3.2 Introduction .......................................................................................................... 75
3.3 Experimental and Computational Techniques ...................................................... 76
3.4 Experimental Results and Discussion .................................................................... 78
3.5 Computational Results and Discussion ................................................................. 83
3.6 Conclusion .......................................................................................................... 86
3.7 Figures ................................................................................................................. 87
3.8 Acknowledgments ............................................................................................. 98

**Chapter Four** Electronic Properties of Adsorbates on In_{0.37}Ga_{0.63}As(001)-(2×4) ............... 99

4.1 Abstract ................................................................................................................. 99
4.2 Introduction .......................................................................................................... 100
LIST OF SYMBOLS AND ABBREVIATIONS

Aluminum  
Angstrom  
Arsenic  
Auger Electron Spectroscopy  
Capacitance Voltage  
Celsius  
Centimeter  
Chlorine  
Current  
Degree  
Density Functional Theory  
Density of States  
Electron  
Electron Volt  
Enthalpy of Adsorption  
Et Alia  
Gadolinium  
Gallium  
Germanium  
Germanium on Insulator  
Hour  
Hydrogen  
Indium  
Low Energy Electron Diffraction  
Metal Oxide Field Effect Transistor  
Minute  
Monolayer  
Nanoampere  
Nanometer  
Nitrogen  
Oxygen  
Perdew-Burke-Ernzerhof  
Perdew-Wang 1991  
Phosphorus  
Projected Density of States  
Projector Augmented Wave  
Sample Voltage  
Second  
Al 
Å 
As 
AES 
CV 
C 
cm 
Cl 
I 
o 
DFT 
DOS 
e

eV 
ΔH 
et al.
Gd 
Ga 
Ge 
GOI 
h 
H 
In 
LEED 
MOSFET 
min 
ML 
nA 
nm 
N 
O 
PBE 
PW91 
P 
PDOS 
PAW 
Vs 
s
<table>
<thead>
<tr>
<th>Term</th>
<th>Abbreviation</th>
</tr>
</thead>
<tbody>
<tr>
<td>Silicon</td>
<td>Si</td>
</tr>
<tr>
<td>Scanning Tunneling Microscopy</td>
<td>STM</td>
</tr>
<tr>
<td>Scanning Tunneling Spectroscopy</td>
<td>STS</td>
</tr>
<tr>
<td>Tunneling Current</td>
<td>$I_t$</td>
</tr>
<tr>
<td>Ultra High Vacuum</td>
<td>UHV</td>
</tr>
<tr>
<td>Vienna \textit{ab initio} Simulation Package</td>
<td>VASP</td>
</tr>
<tr>
<td>Versus</td>
<td>vs.</td>
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<tr>
<td>Volt</td>
<td>V</td>
</tr>
</tbody>
</table>
# LIST OF FIGURES

## Chapter One Figures

<table>
<thead>
<tr>
<th>Figure</th>
<th>Description</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.1</td>
<td>STM image and ball-and-stick diagram of clean GaAs(001)-c(2×8)/(2×4) surface</td>
<td>28</td>
</tr>
<tr>
<td>1.2</td>
<td>STM images and ball-and–stick diagrams of GaAs(001)-c(2×8)/(2×4) after SiO deposition</td>
<td>29</td>
</tr>
<tr>
<td>1.3</td>
<td>STS measurements of the clean and SiO deposited GaAs(001)-c(2×8)/(2×4) surface</td>
<td>31</td>
</tr>
<tr>
<td>1.4</td>
<td>Ball-and-stick diagrams depicting electron movement during SiO adsorption to GaAs(001)-c(2×8)/(2×4)</td>
<td>32</td>
</tr>
<tr>
<td>1.5</td>
<td>Chemical potential plots of the SiO bonding sites</td>
<td>33</td>
</tr>
<tr>
<td>1.6</td>
<td>Bond angles, lengths, and relative atomic charges of the SiO bonding sites</td>
<td>35</td>
</tr>
<tr>
<td>1.7</td>
<td>STM simulations of the SiO adsorption sites on GaAs(001)-(2×4)</td>
<td>36</td>
</tr>
<tr>
<td>1.8</td>
<td>DOS of SiO single sites</td>
<td>37</td>
</tr>
<tr>
<td>1.9</td>
<td>DOS of SiO compact double sites</td>
<td>38</td>
</tr>
<tr>
<td>1.10</td>
<td>DOS and PDOS of SiO trough triple site</td>
<td>39</td>
</tr>
<tr>
<td>1.11</td>
<td>DOS and PDOS of SiO trough pyramid site</td>
<td>40</td>
</tr>
</tbody>
</table>

## Chapter Two Figures

<table>
<thead>
<tr>
<th>Figure</th>
<th>Description</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>2.1</td>
<td>Adsorption energies along with ball-and-stick diagrams of the O₂ bonding sites on GaAs(001)-(2×4)</td>
<td>64</td>
</tr>
<tr>
<td>2.2</td>
<td>Adsorption energies along with ball-and-stick diagrams of the In₂O bonding sites on GaAs(001)-(2×4)</td>
<td>65</td>
</tr>
</tbody>
</table>
Figure 2.3 Adsorption energies along with ball-and-stick diagrams of the Ga$_2$O bonding sites on GaAs(001)-(2×4) .......................66

Figure 2.4 Adsorption energies along with ball-and-stick diagrams of the SiO bonding sites on GaAs(001)-(2×4) ...........................67

Figure 2.5 STS and DOS of the clean GaAs(001)-c(2×8)/(2×4) surface ...68

Figure 2.6 STS, DOS, and PDOS of O$_2$/GaAs(001)-c(2×8)/(2×4) ............69

Figure 2.7 STS and DOS of In$_2$O/GaAs(001)-c(2×8)/(2×4) ................70

Figure 2.8 STS and DOS of Ga$_2$O/GaAs(001)-c(2×8)/(2×4) ..............71

Figure 2.9 STS, DOS, and PDOS of SiO/GaAs(001)-c(2×8)/(2×4) ..........72

Chapter Three Figures

Figure 3.1 Ball-and-stick diagrams of possible InAs(001)-(4×2) surfaces .................................................................................87

Figure 3.2 Filled and empty state STM images of the InAs(001)-c(8×2)/(4×2) surface .................................................................88

Figure 3.3 Energetically degenerate $\alpha 2(4\times 2)$ structures ..................................................89

Figure 3.4 Filled and empty state STM images of a commonly seen trough defect on InAs(001)-c(8×2)/(4×2) .........................90

Figure 3.5 Ball-and-stick diagram of the proposed defect site ..........91

Figure 3.6 Atomically resolved STM image of the row structure on InAs(001)-c(8×2)/(4×2) .........................................................92

Figure 3.7 Ball-and-stick diagrams of the $\beta 3(4\times 2)$ and $\beta 3(4\times 2)'$ reconstructions ................................................................93

Figure 3.8 STM images of the clean InAs(001)-c(8×2)/(4×2) surface and the surface after Cl deposition .................................94
Figure 3.9  Top down views of the β3(4×2) and β3(4×2)’ computational slabs ................................................................. 95

Figure 3.10  Filled and empty state STM simulations of the β3(4×2) and β3(4×2)’ structure along with experimental images .............. 96

Figure 3.11  β3(4×2) and β3(4×2)’ bonding angles and lengths................. 97

Chapter Four Figures

Figure 4.1  Side and top views of four different In_{0.37}Ga_{0.63}As(001)-(2×4) computational slabs .................... 110

Figure 4.2  DOS of four different In_{0.37}Ga_{0.63}As(001)-(2×4) slabs with random In and Ga placements ................................. 112

Figure 4.3  Ball-and-stick diagram of the different In_{2}O and Ga_{2}O bonding sites on In_{0.37}Ga_{0.63}As(001)-(2×4) ..................... 113

Figure 4.4  DOS of In_{2}O/In_{0.37}Ga_{0.63}As(001)-(2×4) .................................................. 114

Figure 4.5  DOS of Ga_{2}O/In_{0.37}Ga_{0.63}As(001)-(2×4) ................................. 115
LIST OF TABLES

Chapter One Tables

Table 1.1 Enthalpies of adsorption for row SiO sites .................................. 41

Table 1.2 Enthalpies of adsorption for trough SiO sites ............................. 42

Chapter Four Table

Table 4.1 Summery of In$_2$O and Ga$_2$O bonding properties on GaAs and In$_{0.37}$Ga$_{0.67}$As .............................................................. 116
PREFACE

Over the last three decades many attempts mostly unsuccessful, have been made to construct a III-V metal oxide semiconductor field effect transistors (MOSFET) devices.\textsuperscript{1-10} The potential advantages of these devices include lower power consumption and higher gain than commercially available Si MOSFETs. Three appropriate channel materials for these devices are GaAs, InAs, and InGaAs. When constructing a Si MOSFET device, Si is exposed to an oxidizing atmosphere (O, O\textsubscript{2}, O\textsubscript{3}, and H\textsubscript{2}O) and the resulting oxide, SiO\textsubscript{2}, leaves the Fermi level unpinned.\textsuperscript{11} However, when GaAs, InAs, or InGaAs are exposed to the same oxidizing agents bands bend, pinning the Fermi level, which makes the device inoperable.\textsuperscript{12,13} Therefore, it becomes necessary to find a new oxide for each material that leaves the Fermi level unpinned. An in depth understanding of the oxide pinning mechanisms on III-V semiconductors can help identify appropriate oxides for other III-V semiconductors. To fully understand the oxide/semiconductor interface an atomistic understanding of both the surface reconstruction of the semiconductor and the semiconductor/oxide interface are needed.

Chapter one presents an in depth study of the correlation between atomic bonding sites and the electronic structure of molecular SiO on GaAs(001)-c(2×8)/(2×4). In this study, detailed scanning tunneling microscopy (STM) images and scanning tunneling spectroscopy (STS) spectra are presented. STM images reveal
six different SiO bonding geometries. In addition, the STS spectra show that the Fermi level is pinned midgap at ~5% monolayer (ML) coverage. Density functional theory (DFT) calculations confirmed the experimental findings and helped elucidate the causes of the Fermi level pinning. The Fermi level pinning was found to have either a direct (local charge buildup, and/or partially-filled dangling bonds on Si atoms) or indirect (undimerized surface As atoms) mechanism.

Chapter two compares and contrasts the electronic effects of a wide range of adsorbates on GaAs(001)-c(2×8)/(2×4), including O₂, In₂O, Ga₂O, and SiO. STS measurements revealed that the only adsorbate that left the Fermi level unpinned was Ga₂O. DFT calculations were employed to help deduce the cause of the Fermi level pinning observed for the other three adsorbates. Two distinct pinning mechanisms were found: direct and indirect Fermi level pinning. O₂ was found to pin the Fermi level indirectly on GaAs(001)-c(2×8)/(2×4), while In₂O was found to pin the Fermi level directly. In the case of SiO chemisorbed to GaAs(001)-c(2×8)/(2×4) both pinning mechanisms were present.

The electron mobility of InAs is ~3.8 times greater than GaAs, making it a more promising material than GaAs for a high gain MOSFET device.¹⁴ However, there are very few publications showing an atomic understanding of InAs; even the InAs surface reconstructions are not well understood. Therefore, before attempts can be made to understand the interactions between adsorbates and the InAs surface it is necessary to identify the InAs(001)-(4×2) surface reconstruction. Chapter three
focuses on this task. Detailed STM images, along with DFT calculations, identified the InAs(001)-(4×2) reconstruction as the undimerized β3(4×2) reconstruction.

Although the electron mobility of InAs is ~3.8 times greater than GaAs, the band gap of InAs is only 0.36 eV, causing a significant number of electrons to be promoted from the valence band maximum to the conduction band at room temperature. Although this device would be higher gain than a GaAs device it would also have higher standby power, which is not always desirable. Combining InAs and GaAs gives a material with a higher mobility than GaAs but a larger band gap than InAs, enabling a low power high gain device to be constructed. Chapter four outlines a computational study of In2O and Ga2O bonding to In0.37Ga0.63As(001)-(2×4). The results show that In2O and Ga2O bonding to In0.37Ga0.63As(001)-(2×4) is similar to In2O and Ga2O bonding to GaAs(001)-(2×4). However, some substantial differences exist between the two systems. The most significant difference between the two systems is that it takes more adsorbates bonded in close proximity before states are induced at the band gap edges for In0.37Ga0.63As(001)-(2×4) than for GaAs(001)-(2×4). This difference is attributed to the fact that In0.37Ga0.63As(001)-(2×4) has a smaller band gap than GaAs(001)-(2×4).
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Throughout my PhD program I have been surrounded by individuals who have helped me to progress in my program. Without their help this would not have been possible.

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Outside of work I also have a strong support group of family and friends that I would like to acknowledge. I would like to thank my Dad for giving me the love for science that got me here. In addition, I would like to thank my Mom for her encouragement and support. Lastly, I would like to thank Alex Feldman who spent many hours proofreading papers, listing to upcoming presentations, and giving me an extra hand when I needed it.

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D.L. Winn, T.J Grassman, and A.C. Kummel “Electronic Properties of Adsorbates on In0.37Ga0.63As(001)-(2×4),” In preparation for submission to *ECS Transactions*. Chapter 4
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8. The Physics and Chemistry of Semiconductor Interfaces (poster 2003): “Understanding Fermi Level Pinning of SiO on GaAs(001)-(2×4)”

Publications
1. D.L. Winn, J. Shen, J.B. Clemens, T.J. Grassman, and A.C. Kummel “Definitive Identification of the InAs(001)-c(8×2)/(4×2) Reconstruction” In preparation for submission to Surface Science.
2. D.L. Winn, T.J. Grassman, and A.C. Kummel “Electronic Properties of Adsorbates on In0.37Ga0.63As(001)-(2×4)” In preparation for submission to ECS Transactions.
Field of Study
Major Field: Chemistry (Physical Chemistry)
Studies in Surface Science
Professor Andrew Kummel

Major Field: Chemistry (Physical Chemistry)
Studies in Surface Science
Professor Steven Buratto
ABSTRACT OF THE DISSERTATION

PROPERTIES OF ADSORBATED ON III-V SEMICONDUCTORS

by

Darby L. Winn

Doctor of Philosophy in Chemistry

University of California, San Diego, 2007

Professor Andrew Kummel, Chair

In order to develop a III-V MOSFET device it is important to have an atomic understanding of both the clean III-V surface reconstruction and the interface formed when an adsorbate is deposited onto the surface. Three promising channel materials for a III-V MOSFET devices are GaAs, InAs, and InGaAs. In an effort to obtain an atomic understanding of the III-V materials and the interfaces that form when adsorbates bond to them, three critical techniques [scanning tunneling microscopy (STM), scanning tunneling spectroscopy (STS), and density functional theory (DFT)] were employed. STM was used to characterize the adsorbate/semiconductor interface along with identifying previously undetermined surface reconstructions. The electronic properties of the system were examined by taking STS spectra, which reveal how the adsorbate changes the electronic properties of the semiconductor after bonding. In addition, DFT was used to confirm experimental results along with predicting other adsorbate/semiconductor interactions.
CHAPTER ONE

Direct and Indirect Causes of Fermi Level Pinning at the SiO/GaAs Interface

1.1 Abstract

The correlation between atomic bonding sites and the electronic structure of SiO on GaAs(001)-c(2×8)/(2×4) was investigated using scanning tunneling microscopy (STM), scanning tunneling spectroscopy (STS), and density functional theory (DFT). At low coverage, STM images reveal that SiO molecules bond Si end down; this is consistent with Si being under coordinated and O being fully coordinated in molecular SiO. At ~5% ML (monolayer) ML coverage, multiple bonding geometries were observed. To confirm the site assignments from STM images, DFT calculations were used to estimate the total adsorption energies of the different bonding geometries as a function of SiO coverage. STS measurements indicated that SiO pins the Fermi level midgap at ~5% ML coverage. DFT calculations reveal that the direct causes of Fermi level pinning at the SiO GaAs(001)-(2×4) interface are a result of either local charge buildups or the generation of partially filled dangling bonds on Si atoms.
1.2 Introduction

Early attempts to fabricate a GaAs-based metal-oxide semiconductor field-effect transistor device focused on using either SiO$_2$$^{7,16-19}$ or the native oxide of GaAs$^{3,8,20}$ as the gate dielectric. Unfortunately, both oxides were found to induce states within the band gap, pinning the Fermi level.$^{21-23}$ The Fermi level is considered pinned when an external potential can no longer modulate the Fermi level position making a device inoperable. In the case of GaAs’s native oxide, Fermi level pinning was initially attributed to excess As on the surface,$^{24-28}$ but an atomic level understanding of the oxide/GaAs interface did not exist. Since the two conventional oxides (SiO$_2$ and the native oxide) pin the Fermi level, a broad search of other oxides was needed to find a gate dielectric material that would passivate the GaAs surface, leaving the Fermi level unpinned.

In an effort to find an appropriate oxide, research efforts have recently shifted to include not only macroscopic studies [capacitance voltage (CV), photoluminescence, etc.] but also microscopic studies [scanning tunneling microscopy (STM) and scanning tunneling spectroscopy (STS)]. These microscopic studies (Hale et al.$^{29,30}$ and Negoro et al.$^{31}$) have given insight into the atomic structures of adsorbates bound to the GaAs(001)-c(2×8)/(2×4) surface and revealed that the cause of the Fermi level pinning was not excess As on the surface.
Several macroscopic studies have been performed on the SiO/GaAs interface, but none on the atomic level. Building on previous work, the results presented in this manuscript show how the exact atomic placement of SiO adsorbates influences the electronic structure of SiO/GaAs(001)-c(2×8)/(2×4) system.

1.3 Experimental Techniques

Experiments were performed in an UHV chamber with a base pressure of $3 \times 10^{-10}$ Torr. The chamber is equipped with low energy electron diffraction (LEED) and a Park Scientific AutoProbe VP STM with STS capabilities. As$_2$-capped (~25 nm) $n$- and $p$-type molecular beam epitaxially grown GaAs samples were used for the study, with Si and Be dopant concentrations of $2 \times 10^{17}$ cm$^{-3}$, respectively. Both $n$- and $p$-type samples appear identical in STM images but differ in electronic properties.

To prepare the samples for STM, a thermal decapping procedure was employed. Initially, the samples were degassed at 200ºC for at least 2 h to remove the weakly bound adsorbates such as water. This was followed by 10-50 cycles of 2 min temperature ramps to 420ºC followed by instantaneous drops in temperature and stabilization at 50ºC for another 2 min, to remove the As$_2$ cap. These cycles were repeated until there was no pressure rise due to As desorbing from the surface. A plot of the temperature ramps and subsequent pressure rises can be found on EPAPS. Following the decapping procedure, the surface order was verified by both LEED and
STM. Variable tip-sample separation STS ($dI/dV$) measurements were taken utilizing an ac modulated input signal and a lock-in amplifier. STS was used to confirm that the clean surface was unpinned.

Once the atomic and electronic structures of the clean GaAs(001)-c(2×8)/(2×4) surface were characterized, the samples were dosed with molecular SiO. The SiO was deposited from sintered SiO powder heated to 950°C in a differentially pumped effusion cell. SiO powder has been shown to evaporate congruently as molecular SiO with no other oxide species, at low evaporation temperature and pressure, similar to our operating conditions. The deposition was performed at a main chamber pressure of ~2×10$^{-8}$ Torr with the sample held at ~14°C; postdeposition anneals were found to have no influence on the bonding geometries. After SiO deposition, STM and STS measurements were again used to characterize the surface.

1.4 Experimental Results and Discussion

A. Scanning tunneling microscopy images and line scans

Figure 1(a) is a filled-state STM image of the clean GaAs(001)-c(2×8)/(2×4) surface. The bright rows that run in the [110] direction are comprised of first-layer electronegative As dimer pairs. A ball-and-stick diagram of the GaAs(001)-(2×4) surface is provided in Fig. 1(b). The As dimers that reside in the troughs are not
resolved with these imaging conditions due to tunneling between the trough edge atoms and the tip, prohibiting the tip from fully entering the trough.\textsuperscript{47}

The actual GaAs(001) surface structure is a mixture of the \(c(2\times8)\) and \(2\times4\) surface reconstructions.\textsuperscript{41,47} The difference between the two reconstructions is subtle: in the \(c(2\times8)\) surface structure, consecutive As dimer rows are staggered by \(\frac{1}{2}\) of a unit cell along the \([\bar{T}10]\) direction, instead of lining up across the trough, as seen in the \(2\times4\) reconstruction. However, both structures have the same electronic properties and few defects (< 2%). The two most common imperfections (missing As dimers and excess As) observed via STM are a result of the thermal decapping procedure. Missing As dimers result from the surface getting slightly too warm and are depicted in the ball-and-stick diagram in Fig. 1(b). Excess As is the most common imperfection and occurs from the nonuniform heating of the sample and is imaged as bright patches on the dimer rows.

Once the clean surface has been confirmed using LEED and STM, SiO is deposited. Figure 2(a) shows a large-scale image of the GaAs surface after depositing SiO for 1 min on room-temperature GaAs(001)-\(c(2\times8)/(2\times4)\), resulting in \(\sim 5\%\) ML coverage. The bright patches on the rows and troughs are the SiO bonding sites, some of which have been encircled in black. SiO is not confused with excess As because the latter generally forms clumps which span several rows. A magnified STM image showing three different SiO bonding sites is presented in Fig. 2(b); line scan analysis was performed on the STM image to help deduce the bonding sites. Figure 2(c) (top)
is a line scan of the adsorption site (bright patch) in the upper left hand corner of Fig. 2(b): this site images 4 Å long and 1.5 Å tall. It is proposed that this site consists of one SiO molecule inserting into an As dimer, denoted as a “single site.” A side-on model of the proposed row single site is shown under the line scan in Fig. 2(c) (top) and a top-down view is seen in Fig. 2(f) (site 1). The other experimentally observed row site is seen in the bottom center of Fig. 2(b). Line scan analysis [Fig. 2(c) (bottom)] reveals that this site measures twice as long in the [110] direction as the single site and is of the same height. This site is proposed to be a “compact double site,” which consists of a SiO molecule inserting into an As dimer and an additional SiO molecule inserting between the insertion dimer and an adjacent dimer. A side-on model of the row compact double site is seen under the line scan in Fig. 2(c) (bottom) and a top-down model of the site is shown in Fig 2(f) (site 2).

Both of the sites observed on the row are also proposed to occur in the trough region, in addition to two unique trough sites. Three of the trough sites (single, compact double, and triple sites) are not casually observed in the STM images. This is due to the lack of trough resolution at these tunneling conditions, as discussed previously. These sites, however, can be characterized by line scan analysis. Line scan analysis shows that the trough single [Fig. 2(d) (top)] and the trough compact double [Fig. 2(d) (middle)] are the same length in the [110] direction as the corresponding sites on the row. Side-on models of the single and compact double sites are seen under their line scans. The third type of trough site, also observed only by
line scan analysis, has no row-type analogue and measures 12 Å long in the \([\bar{1}01]\) direction [Fig. 2(d) (bottom)]. This site is proposed to be two SiO molecules inserting into adjacent dimers and a third SiO molecule inserting between them; this site is denoted as a “triple site.”

Another site that is only observed in the trough is shown via a side-on model in Fig. 2(e). Unlike the trough sites in Fig. 2(d), the site in Fig. 2(e) is consistently observed in experimental STM images. This site measures ~1 Å higher than the row, which is too tall to be a simple insertion site (i.e., it must contain stacked SiO molecules). Although such a conclusion cannot be reached exclusively from STM images, this site is proposed to be a “pyramid site.” Other data will be presented that will further substantiate this site assignment. Side-on models along the \([110]\) and \([\bar{1}10]\) directions, along with line scans of the pyramid site, are seen in Fig. 2(e). In addition, a top-down model of the pyramid site is shown in Fig. 2(f) (site 4).

The STM images strongly suggest that SiO bonds Si end down, which is consistent with simple chemical principles. The valence shell of a Si atom contains four electrons and is sp\(^3\) hybridized, therefore, it typically forms four bonds. An O atom contains six valence electrons and typically forms only two bonds, leaving two filled dangling bonds (i.e., two lone pair orbitals). Assuming that SiO inserts Si end down, Si can form one bond with each of the surface As atoms in the dimer and form a double bond with the O atom. This allows both the O atom and the Si atom to satisfy the requirements of the octet rule.
The 1.5 Å height difference observed by STM between the SiO molecule and the dimer row (seen in the row single and compact double sites) is also consistent with SiO inserting Si end down. The images obtained from STM are a convolution of atomic position, local density of states, and electron density. If SiO inserts Si end down, the majority of the most weakly bound electron density (i.e., closest to the Fermi level) should be concentrated in the double bond between the Si and O since the highest occupied molecular orbital is concentrated in that area. For SiO bonded Si end down, the double bond should be approximately 1.5 Å above the As dimer row, which is in agreement with the experimental observations. Furthermore, the electron density in the filled dangling bonds of the O atoms have an energy level far below the Fermi level, prohibiting electrons from tunneling out of those orbitals and into the tip.\textsuperscript{30,48,49} If SiO were to insert O end down, the majority of the electron density near the Fermi level would be concentrated in the nonbonding orbitals of Si. This would result in a taller site than is experimentally observed.

The trough sites (single, compact double, triple, and pyramid sites) are expected to image at two different heights. In structural models, the trough is ~3 Å deep. However, experimentally the average trough depth is ~1.5 Å, therefore, anything below this height will not be directly observed. Since the trough single, compact double, and triple sites are only expected to image at ~1.5 Å from the bottom of the trough, one would not expect these sites to have prominent features in STM images, which is consistent with the STM data shown in Fig. 2(d). In contrast, the top double bond in the trough pyramid site is located ~3 Å from the bottom of the trough;
therefore, one might expect the trough pyramid site to image level with the row (since the trough is ~3 Å deep). Experimentally the trough pyramid site is found to image ~1 Å above the row, slightly higher than one might predict. The height difference between the predicted and actual image height is attributed to the top O atom having a greater density of states at an energy closer to the Fermi level than a typical surface O atom (as will be discussed later in the paper). Therefore, unlike most surface O atoms, the top O atom in the trough pyramid site is imaged, resulting in the trough pyramid site imaging ~1 Å above the row.

B. Scanning tunneling spectroscopy

In addition to the STM images of the various SiO adsorption sites, STS (surface electronic structure) measurements were also taken using the variable tip-sample separation method developed by Feenstra and co-workers. With this technique, GaAs(001) was found to have a band gap of 1.4 V. Figure 3(a) presents \( \frac{dI}{dV}(\frac{1}{V}) \) vs V spectra [which are proportional to the density of states (DOS)] for clean \( n \)- and \( p \)-type GaAs(001)-c(2×8)/(2×4) surfaces respectively. The Fermi level for all given \( \frac{dI}{dV}(\frac{1}{V}) \) curves resides at 0 V. From the data, it can be seen that the Fermi level for \( n \)-type GaAs(001)-c(2×8)/(2×4) resides near the conduction band and the Fermi level for \( p \)-type GaAs(001)-c(2×8)/(2×4) resides near the valence band, as expected. These results are typical of unpinned \( n \)- and \( p \)-type surfaces. Figure 3(b) shows STS spectra that were taken after depositing ~5% ML SiO on \( n \)-
and $p$-type GaAs(001)-c(2×8)/(2×4), respectively. In both cases, the bands are shifted, relocating the Fermi level to midgap; this is consistent with a pinned surface, indicating that Fermi level pinning occurs at SiO coverages as small as ~5% ML.

From the ball-and-stick diagram in Fig. 2(f), it can be seen that none of the proposed sites liberate As when SiO is deposited onto the surface. Furthermore, from the STM image in Fig. 2(a), no excess As deposits are seen. Therefore, excess As is certainly not the cause of the Fermi level pinning in this case.

C. Local charge buildup model

To deduce the cause of the Fermi level pinning, a closer look is taken at the transfer of electrons during SiO bonding to the surface using simple molecular orbital models. The bonding electrons of the system are located in the tetrahedral ($sp^3$ hybridized) orbitals of the As and Si atoms. Prior to bonding with the surface, the Si atom in a SiO molecule has two half-filled dangling bonds. In order to calculate a minimum number of electrons in the dangling bonds of the surface As atoms, the rules of the standard electron counting model are applied. These rules state that atoms contribute the same number of electrons to surface bonds as they do in the bulk material (i.e. As gives 5/4 of an electron to Ga in the bulk, therefore it gives 5/4 of an electron to a bond with a surface Ga atom) and atoms bonded to like atoms each give one electron to the bond. Therefore, since the dimer As atoms are each bonded to
two Ga atoms and one As atom, the dangling bond on dimer As atoms are left with at least 3/2 electrons.

Figure 4(a) is a ball-and-stick diagram depicting the formation of a single site, with arrows denoting the movement of electrons. In the formation of the single site, the SiO molecule inserts into the As-As bond and forms two new Si-As bonds with the surface. Each time an As-As bond is broken, each As atom gains one electron. In order to form a Si-As bond, the bond receives one electron from the dangling bond in Si and one electron from the As atom. The number of electrons needed to form the bond is exactly equal to the number of electrons available between the Si and As atoms (i.e., two electrons); therefore, no buildup of extra electrons, or local charge, on any of the atoms associated with this adsorption site is expected.

Unlike the single site, the compact double site is expected to have a small local charge buildup. The formation of the compact double site is shown in Fig. 4(b). When a compact double site forms, one SiO molecule inserts into an As dimer and the other SiO molecule inserts between that same dimer and the neighboring As dimer. The distal As atom in the neighboring dimer (that is not involved in the SiO bonding) may redimerize if the energy barrier is low enough. In the formation of the compact double site, four Si-As bonds are created. The center As atom is forced to form a total of four bonds (two Ga-As and two Si-As); therefore, the As atom can no longer have any dangling bonds. Since the preexisting dangling bond had 3/2 electrons, an excess of ½ of an electron remains after the formation of the Si-As bonds. This excess ½ of
an electron may then be incorporated into the local bond network and/or the partially filled dangling bonds on the outer As atoms, potentially giving the dangling bonds a minimum charge of $7/4$ electrons, as seen in Fig. 4(b).

The triple and pyramid sites are expected to have larger local charge buildup, as depicted in Figs. 4(c) and 4(d), respectively. In the case of the triple site, three SiO molecules form six Si-As bonds with the surface [Fig. 4(c)]. Since the center two As atoms can no longer have dangling bonds, there remains an excess charge of one electron that must be incorporated into the local system, which can result in the outer As atoms’ dangling bonds possessing a minimum of two electrons each. This local charge buildup should be large enough to perturb the local electronic structure and potentially pin the Fermi level.

The pyramid site is the most complicated SiO adsorption site. From Fig. 4(c), it can be seen that there are two major sources of charge buildup. The first source is the center As atom that forms two Si-As and two Ga-As bonds, similar to the compact double site. This generates an excess of $\frac{1}{2}$ electron that needs to be incorporated into the local system (i.e. bond network and/or outer As atoms’ dangling bonds). The second source of charge buildup occurs as a result of the undercoordination of the bottom Si atoms. In the SiO pyramid, the bottom O atoms are single bonded to two different Si atoms (as opposed to being double bonded to a single Si atom as in all of the other adsorption geometries). Therefore, the bottom Si atoms are $sp^3$ hybridized while all of the other Si atoms are $sp^2$ hybridized. Since the bottom Si atoms form
three fully formed bonds (one Si-O and two Si-As) they have an additional half-filled dangling bond. These half-filled dangling bonds are predicted to generate a state in the band gap region, thereby pinning the surface.

This simple model implies that there may be two distinct direct causes of Fermi level pinning in the SiO/GaAs(001)-c(2×8)/(2×4) system: the buildup of local charge (triple site) and partially filled dangling bonds on Si atoms (pyramid site). The validity of the local charge buildup model is further examined with DOS, projected density of states (PDOS), and atomic charge analysis from density functional theory (DFT) calculations.
1.5 Computational Results and Discussion

A. Enthalpies of adsorption

Plane-wave (periodic boundary) DFT calculations were performed with the Vienna \textit{ab initio} simulation package (VASP) code\textsuperscript{51-54}. The surface of interest was modeled using an eight layer GaAs(001) H-terminated slab with the (2×4) surface reconstruction. The bottom four layers of the slab were frozen to help simulate bulk properties. The calculations were performed using the Perdew-Burke-Ernzerhof\textsuperscript{55} (PBE) variant of the general gradient approximation. Projector augmented wave (PAW) potentials were used to represent the atoms (as supplied with VASP)\textsuperscript{56,57}. The plane wave cutoff energy was set to 400 eV, and the $k$-point sampling utilized was a 4×4×1 Monkhorst-Pack\textsuperscript{58} $k$-point sampling scheme resulting in a total of four irreducible $k$-points in the first Brillouin zone. The structures were considered adequately relaxed once the interatomic forces were below 0.01 eV/Å.

The errors associated with these calculations are not straightforward to estimate. There are two types of errors that arise in DFT calculations: convergence errors and method errors. Convergence errors include both errors related to the choice of convergence parameters (plan-wave cutoff, $k$-points, slab thickness, vacuum thickness, etc.) as well as relaxation parameters (maximum allowed forces on atoms). If the appropriate computational parameters are chosen, the convergence errors should
be negligible compared to the method errors. The method errors encompass the errors inherent to the chosen computational method (exchange correlation functional, various approximations, atomic potential, etc.) and can be further broken down into two subcategories: absolute method errors and relative method errors (or uncertainties).

Absolute method error refers to how well the computational results match with experimental data. Paier et al. calculated the mean absolute error (absolute method error), with respect to experimental values, of the G2-1 test set as 0.37 eV using VASP, with PAW potentials and the PBE exchange correlation functional\textsuperscript{59} (the same as was used in the work presented here). Although the absolute method error was calculated for a large set of widely varying molecular systems (55 in total), the test set does not include any adsorbates on surface, which would be closer to the systems in the current study. Additional literature searches revealed no systematic studies of absolute method errors for adsorbates on surfaces. Although the absolute method error in this study is potentially as large as 0.37 eV, the relative method errors are expected to be much smaller.

The relative method error refers to the uncertainty in the total energy difference between two similar adsorption sites. When comparing the relative total energies of a single adsorbate at two different sites on a surface, the relative error is the most important error. For example, if the relative method uncertainty is $\pm 0.10$ eV and two structures, both having one adsorbate bonded in different locations, have adsorption energies of 1.00 and 1.05 eV then the two structures are considered to be
degenerate due to computational uncertainties. A search of the literature revealed no systematic study of the relative method error for adsorbates on surfaces. However, experts in the field report differences in binding energy at similar absorption sites on the same surface of $\pm 0.10$ eV to be significant using computational techniques similar to the ones in the present manuscript. Therefore, we will assume a relative method error of $\pm 0.10$ eV in the current study. Since the differences in calculated absorption energy are usually much larger than $\pm 0.10$ eV, the overall qualitative trends in both the calculations and the experiments should be in good agreement.

Both experimentally observed and nonobserved (but chemically possible) sites were modeled in an effort to verify the bonding geometries that were deduced from STM images. Tables I and II show top-down views of the calculated row and trough bonding sites, respectively, and include their corresponding enthalpies of adsorption, enthalpies of adsorption per SiO, and corrected enthalpies of adsorption per SiO (in structures that have an undimerized As atom). In order to calculate the row As dimerization energy, two clean slabs with eight row As atoms were modeled: one with the row As atoms dimerized, and the other with row As atoms undimerized. The energy difference between these two slabs amounts to four times the As dimerization energy. A similar calculation was performed to calculate the trough dimerization energy.

The DFT total energy calculations show that many of the row and trough sites are nearly energetically degenerate (Tables I and II). All of the sites that are nearly
degenerate come from having two single sites in immediate proximity of each other (i.e., two SiO atoms in adjacent dimers in the [110] or [\(\bar{1}10\)] direction which are referred to as the “horizontal double” and “vertical double,” respectively). Therefore, it is only necessary to present calculations for the row and trough single sites throughout the rest of the paper.

The row/trough compact double sites were found to be less stable than the row/trough single sites by \(~0.24\) eV per SiO. In the row, the compact double site has a total corrected \(\Delta H_{\text{ads}}\) of \(-1.74\) eV (double the corrected value of \(-0.87\) eV/SiO from Table I). The compact double site is a combination of a single site and an insertion site between As dimers. Since the row compact double site receives \(-1.08\) eV of stability from the single site, it is deduced that the insertion site between As dimers only provides a \(-0.66\) eV gain in stability. However, in the trough, the compact double site has a total corrected enthalpy of reaction of \(-2.12\) eV; therefore, it receives an additional \(-0.80\) eV of stabilization from the addition of the second SiO molecule between the dimers. Since the compact double site is the building block for sites that contain three SiO molecules (triple and pyramid sites), this data would imply that complexes containing three SiO molecules should be more stable in the troughs than in the rows.

Experimentally, the biggest difference in row and trough sites occurs in sites that have three SiO molecules in them (triple and pyramid sites). On the row, there are no experimentally observed sites that contain three SiO molecules, while in the
trough two different sites with three SiO molecules are experimentally observed. Calculations were attempted on both the row triple and row pyramid sites. The row triple site was found to be significantly less stable than the experimentally observed row sites (single and compact double sites), and the row pyramid site was altogether computationally unstable (i.e., the pyramid consistently fell apart during geometric optimization). In contrast, the trough triple and pyramid sites were found to be stable by DFT calculations. This stabilization is attributed to the Ga atoms that protrude into the trough. An analysis of simple Coulombic potentials indicates that if the Ga atoms that protrude into the trough have as few as $\sim 0.08e^{-}$ in their dangling bonds, then the SiO molecules in the trough receive $\sim 0.1$ eV of stabilization per SiO molecule.

To determine if it is reasonable to assume that trough edge Ga atoms have a charge of $0.08e^{-}$, an atomic charge analysis was performed. For this analysis, the Bader method for the calculation of atomic charges was employed. In this method, the charge density minima around each atom defines where the division of charge between atoms occurs. The charge density encapsulated by these minima are then integrated to yield approximate atomic charges. In order to determine the approximate number of electrons in a dangling bond on an edge Ga atom “relative” atomic charges (the difference in atomic charge between an edge Ga atom and a Ga atom in the bulk) are calculated. The relative charge was found to be $\sim 0.09e^{-}$. Since the number of electrons in the dangling bonds of the Ga atoms that protrude into the
trough is greater than the charge needed to stabilize the trough sites by 0.1 eV per SiO, the trough sites should be expected to be more stable than the row sites.

B. Total energy versus chemical potential

The DFT adsorption energy calculations indicate that the lowest energy structures (per unit SiO) on the row and in the trough are the single sites (see Table I and II). However, the single sites are not the most prevalent sites observed in STM images. In order to reconcile this discrepancy between theory and experiment, the SiO coverage needs to be taken into account. As the SiO coverage increases, the SiO chemical potential increases, altering the most energetically preferred adsorption geometries. A total SiO chemical potential plot was constructed using the method described by Qian and *et al.* and normalized to the appropriate energy range. Figure 5(a) displays the lowest energy row and trough sites on one graph, clearly illustrating the fact that the trough sites are slightly more energetically preferred than the row sites. At first glance, the STM images may suggest that trough sites are not preferred over row sites; however, three of the trough sites (single, compact double, and triple sites) are not readily observed due to the previously discussed trough imaging issue, and therefore, the number of trough sites is always underestimated. Taking this into account, the experimental images are believed to verify that SiO preferentially bonds in the trough and, therefore, agree with the theoretical results in Fig. 5(a).
To study the effects of varying SiO coverage on the stability of row sites, a chemical potential plot including only row sites [Fig. 5(b)] was employed. As SiO coverage increases, the lowest energy site changes from the row single site to the row vertical double site. The row triple site maintains a significantly higher energy than the other structures and would not become the lowest energy structure until the chemical potential of SiO reaches ~0.8 eV. This explains why the row triple site is not observed experimentally.

The effect of SiO coverage in the trough was also explored by constructing a total energy versus chemical potential plot for the trough sites [see Fig 5(c)]. This plot reveals that the lowest energy site in the trough changes from the trough single to the trough vertical double and finally to the trough pyramid site, as the SiO coverage increases.

C. Bond angles and lengths

To verify the local charge buildup model presented in Sec. III C, the SiO bonding angles and lengths were examined for the lowest energy structures in the DFT calculations (Fig. 6). The local charge buildup model (Fig. 4) predicted that all of the Si atoms would be $sp^2$ hybridized except for the two Si atoms in the pyramid site that have partially filled dangling bonds, which were predicted to be $sp^3$ hybridized. The relaxed DFT calculated structures (Fig. 6) reveal that the Si-O bond lengths are all ~1.55 Å, except for the Si atoms in the pyramid site that have partially filled dangling
bonds, which have Si-O bond lengths of 1.64 Å. This is consistent with what was predicted because double bonds are shorter than single bonds. In ideal \( sp^2 \) and \( sp^3 \) bonding structures, the bond angles should be 120° and 109.5°, respectively. In the structures that only contain \( sp^2 \) Si atoms [row single, row compact double, trough single, trough compact double, and trough triple Fig. 6(a)-(e)], the bond angles (As-Si-As and As-Si-O) calculated using DFT only deviate a maximum of 15° from their ideal values. Conversely, in the trough pyramid site, all of the angles greatly deviate from the ideal angles. This suggests that the simple model of having one electron in the dangling bonds on the bottom Si atoms in the pyramid site is oversimplified and some of the charge has redistributed throughout the bonding network as well as into the dangling bond of the Si atom.

**D. Scanning tunneling microscopy simulations**

Tersoff-Hamann-style STM simulations\(^{65}\) of the experimentally observed SiO adsorption sites were performed to further substantiate the assigned bonding geometries. The STM simulations are found in Fig. 7, including top-down views of the structures overlaid on the simulated images. The STM simulations of the row single [Fig. 7(a)], row compact double [Fig. 7(b)], and trough pyramid [Fig. 7(f)] sites are in good agreement with experiments. However, the simulated trough single [Fig. 7(c)], trough compact double [Fig. 7(d)], and trough triple [Fig. 7(e)] sites appear much higher/brighter than experimentally observed sites because these simulations do
not account for the physical geometry of the tip. In experiments, the STM tip’s inability to fully enter the trough causes the trough to image much more shallow than found in theoretical structural models ( ~1.5 Å versus ~3.0 Å deep). Therefore, any trough site (single, compact double, or triple site) that is calculated to image at 1.5 Å or below will not be directly observed in STM images but will be readily seen in STM simulations. The STM simulations, along with the total energy versus chemical potential data, confirm that the site assignments from experimental STM images are indeed correct.

E. Density of states and projected density of states

DOS and PDOS calculations were performed on the experimentally observed sites in an effort to elucidate the cause of the Fermi level pinning. These theoretical electronic structures differ slightly from the experimental \( (dI/dV) \) curves because the computational slabs are much too small for the inclusion of dopants and, therefore, are essentially intrinsic GaAs. In addition, the position of the Fermi level between the valence and conduction bands is arbitrary, so for ease of comparison all the DOS and PDOS curves have been aligned at the valence bands. As a result, a modeled surface is considered unpinned if there are no states found to exist between the valence and conduction band edges.
The compact double sites and the trough pyramid site have surface As atoms that are not dimerized in the computational model (experimentally, these atoms may either remain undimerized or, if the energy barrier is low enough, they may redimerize down the row). These undimerized As atoms induce large states within the band gap region. Although the undimerized As atoms might play an indirect role in the Fermi level pinning, it is important to also explore whether the adsorbed SiO molecules themselves play a direct role in the Fermi level pinning. To negate the effects of the undimerized As atoms, H atoms were used to passivate the dangling bonds on the undimerized surface As atoms to simulate As redimerization. Once the H atoms were utilized, the states caused by the undimerized As atoms disappeared, leaving only the states directly induced by the SiO molecules. Both H atoms with a charge of 1 electron and 0.75 electrons were found to passivate the surface. The results from the calculations using one electron H atoms are presented because the electron counting model states that As atoms donate only one electron to bonds with other As atoms.50

The total DOS for the row and trough single sites are given in Fig. 8. The DOS shows that no states reside in the band gap. Therefore, the single sites are expected to leave the Fermi level unpinned.

A summary of the electronic structures for the row and trough compact double sites is given in Fig. 9(a) along with a top-down view of the structures used in the calculations, Fig 9(b) (note: with H passivation). The DOS [Fig. 9(a)] reveals that for the compact double sites, there are no states between the valence band and conduction
band edges. However, the row compact double site has a slightly narrower band gap due to conduction band edge states. Since there are no states in the band gap region the compact double sights is considered to leave the Fermi level unpinned.

A summary of the electronic structures for the trough triple site is presented in Fig. 10. The DOS for the trough triple site shows that a state resides near the conduction band edge [Fig. 10(a)]. PDOS [Fig. 10(c) and 10(d)] calculations reveal that the state generated from the trough triple site resides on the surface As, Si, and O atoms. It is likely that the SiO trough triple site contributes to the experimentally observed Fermi level pinning.

Similar to the compact double site, the formation of the trough pyramid site might also result in the generation of undimerized As atoms. The electronic structure for the H-passivated trough pyramid site is presented in Fig. 11. The DOS [Fig. 11(a)] for the trough pyramid site shows that a double state resides almost in the middle of the band gap. It is possible that the two states might represent an acceptor and a donor state. The PDOS reveals [Fig. 11(c) and 11(d)] that this state extends across multiple atoms. These atoms include the SiO molecules and the As atoms in the trough; however, these states do not extend into the bulk material and are purely surface states.
F. Atomic charge analysis

An atomic charge analysis can be used to quantify the local charge buildup in these adsorption structures and explain the appearance of band gap states in the trough triple and pyramid sites. Atomic charges can be calculated using the Bader method discussed previously. The relative charges are calculated from differences in atomic charges between the clean surface and a surface containing the SiO molecules (Fig. 6). In order to calculate relative charges for the Si and O atoms, the single sites were used as the standard. For row sites the row single was used as the zero point, and for trough sites the trough single was used as the zero point. The total (a sum of the surface As, Si, and O atoms) charge buildup is presented under each of the structures in Fig. 6.

Fig. 6 clearly shows that larger charge buildups occur on the interior As atoms than on exterior ones. This is consistent with what was predicted by the local charge buildup model. A subtlety that was not predicted by the local charge buildup model is that even when no interior As atom is present [as in the case with the single sites, Fig. 6(a) and (c)], SiO still donates small amounts of charge to the surface As atoms; this result is understandable considering the difference in electronegativity between As and Si (2.18 vs 1.90, respectively). Another assumption that the local charge buildup model made was that excess charge would preferentially migrate to the dangling bonds on the exterior As atoms. However, the atomic charge analysis revealed that the dangling bonds could only accommodate some of the extra charge, leaving large charge buildups on the interior As atoms and other Si and O atoms. Therefore, a more
reliable way of quantifying the local charge buildup is by looking at the total charge buildup on all of the surface atoms (As, Si, and O).

Atomic charge analysis can be used to explain why the DOS indicated that the SiO pinned the Fermi level for some of the bonding geometries and left the Fermi level unpinned for other geometries. The DOS suggested that the Fermi level was unpinned for the row and trough single and compact double sites. Figures 6(a) and 6(c) shows that the single sites have a total charge buildup of \(\sim 0.41e^-\). While the compact double sites, Figs. 6(b) and (c), have a total charge buildup of \(\sim 0.66e^-\). The local charge buildup model predicted that there would be an increase in charge every time an additional As atom was added to the SiO bonding system. Following this logic the trough triple site would be expected to have an even larger charge buildup than the compact double sites; the Bader atomic charge analysis verifies this prediction (0.80e\(^-\)). Although the difference in charge buildups between the compact double and triple sites is seemingly small, it leads to a rather large charge buildup in a small region, which probably induces the band edge states seen in the DOS [Fig. 10(c) and 10(d)].

Although the trough pyramid site [Fig. 6(f)] is predicted to have a comparable charge buildup to the trough compact double site, it has an additional problem: the formation of partially filled dangling bonds on the bottom two Si atoms. This can be seen by the large relative charge of 0.34\(e^-\) (per Si) which resides on the bottom Si atoms in the trough pyramid site. This is consistent with Si atom having a partially
filled dangling bond. As previously discussed, the Si-O bond length also indicates the presence of a single bond which would be consistent with a partially filled dangling bond on the lower Si atoms of the trough pyramid site. These partially filled dangling bonds almost certainly create the midgap states in the DOS [Fig. 11(a)].

1.6 Conclusion

Microscopic experimental techniques (STM and STS) and DFT calculations show that the exact bonding geometries of SiO on GaAs(001)-c(2×8)/(2×4) determines the electronic structure. While some of the SiO chemisorption sites leave the Fermi level unpinned, other SiO chemisorption sites pin the Fermi level. The Fermi level pinning in the trough triple and pyramid sites was attributed to two direct causes: the buildup of charge on several consecutive As atoms and/or the formation of partially filled dangling bonds on some of the Si atoms. In addition, some of the bonding sites (row compact double, trough compact double, and trough pyramid sites) might cause indirect pinning by generating undimerized As atoms which were shown to pin the Fermi level. The Fermi level pinning seen when SiO chemisorbs to the GaAs(001) surface is not due to the intrinsic properties of GaAs(001) and SiO but due to the specific bonding geometries at the interface.
FIGURE 1.1 (a) 300 × 300 Å$^2$ filled-state STM image ($V_s$=-3 V, $I_t$=0.2 nA) of a clean GaAs(001)-c(2×8)/(2×4) surface. (b) Ball-and-stick diagram showing the atomic positions of the GaAs(001)-c(2×8)/(2×4) surface reconstruction with one of the most common defects, a missing As dimer, circled in red.
FIGURE 1.2 (a) 300 × 300 Å² filled-state STM image (Vₜ=-3 V, Iₜ=0.2 nA) of the GaAs(001)-c(2×8)/(2×4) surface with ~5% ML coverage of SiO. Some of the SiO bonding sites have been circled in black. (b) 50 × 50 Å² filled-state STM image (Vₜ=-3 V, Iₜ=0.2 nA) of row single, row compact double, and trough pyramid sites. (c) Line scans and ball-and-stick diagrams of the two row sites: the single (top), and compact double (bottom) sites. (d) Line scans and ball-and-stick diagrams of the trough sites that are differentiated using line scan analysis: the single (top), compact double (middle), and triple (bottom) sites. (e) Line scans and ball-and-stick diagrams of the trough pyramid site perpendicular, [110] (top), and parallel, [T10] (bottom), to the trough. (f) Top-down ball-and-stick diagram of some of the most commonly observed SiO adsorptions sites; the sites are labeled as indicated, “1” a row single site, “2” a row compact double site, “3” a trough triple site, and “4” a trough pyramid site.
FIGURE 1.3 STS measurements of (a) clean $n$-type (thick solid line) and $p$-type (gray dashed line) GaAs(001)-c(2×8)/(2×4), and (b) ~5% ML coverage of SiO on $n$-type (thick solid line) and $p$-type (gray dashed line) GaAs(001)-c(2×8)/(2×4). Note that both clean $n$- and $p$-type GaAs(001)-c(2×8)/(2×4) STS plots (a) exhibit electrically unpinned surfaces, while the SiO deposited surfaces (b) are found to be pinned.
FIGURE 1.4 Ball-and-stick diagrams of proposed SiO/GaAs(001)-(2×4) adsorption configurations before and after bonding. Arrows represent electron relocation during bonding. Prior to bonding the dangling bonds on the As atoms contain a minimum of 3/2 electrons. The electrons noted in the dangling bonds after SiO bonding has occurred are also minimum projected values. All excess electrons caused by SiO bonding are placed in available dangling bonds. Electrons that cause a local buildup of charge are circled in red. (a) Single site, which is predicted to have no charge buildup. (b) Compact double site, which is predicted to have a small amount of charge buildup (~1/2 e⁻). (c) Triple site, which is predicted to have a greater charge buildup than the compact double site (1 e⁻). (d) Pyramid site, which is predicted to have the same charge buildup as the compact double site, but in addition causes the formation of two partially filled dangling bonds on the bottom two Si atoms.
FIGURE 1.5 The effect of SiO coverage on adsorption site stability is observed in the total energy vs chemical potential plots. As SiO coverage increases, SiO chemical potential likewise increases. (a) A plot of the most stable row and trough sites, which indicates that trough sites are slightly more stable than row sites. (b) A chemical potential plot of solely row sites, showing that the most stable row site changes from the single to the vertical double site as SiO coverage increases. (c) A chemical potential plot of solely trough sites, showing that the lowest energy site changes from the single to the vertical double and finally to the pyramid site as SiO coverage increases.
FIGURE 1.6 The bond lengths and bond angles for each calculated SiO structures: (a) row single, (b) row compact double, (c) trough single, (d) trough compact double, (e) trough tripl, and (f) trough pyramid sites. Equivalent bond angles and lengths have been averaged. In addition, relative atomic charges are displayed. The relative charges are the difference between the atomic charge on the clean surface and the surface containing the absorbed SiO molecules. The Si and O relative charges are calculated by comparing the charge on the single sites to the charge on the Si and O atoms in the other sites. In addition the total charge buildup is boxed under each structure. Note that all of the Si atoms (except for those in the trough pyramid site) exhibit bonding angles corresponding to sp² hybridization. In addition, charge buildup is smaller on exterior As atoms than on interior atoms.
FIGURE 1.7 STM simulations of experimentally observed sites with top-down models of the structures overlaid on the simulations: (a) row single site, (b) row compact double site, (c) trough single site, (d) trough compact double site, (e) trough triple site, and (f) trough pyramid site.
FIGURE 1.8 DFT calculated DOS for the row single site, trough single site, and clean surface. All DOS have been normalized to 1. These simulations show that the row and trough single sites do not cause states to form within the band gap.
FIGURE 1.9 (a) DOS (normalized to 1) for the row compact double site, trough compact double site, and clean surface. These simulations show that the row and trough compact double sites do not cause states to form within the band gap region. However the band gap is slightly narrower for the row compact double site. (b) Ball-and-stick diagrams of the structures used for the electronic calculation. An H atom is used to passivate the undimerized surface As atom in order to remove the states originating from the undimerized As atom.
FIGURE 1.10 (a) DOS (normalized to 1) for the clean surface and the surface containing the trough triple site. (b) Top-down model of the trough triple site with the atoms labeled that are seen in the PDOS plots. (c) PDOS of the relevant As atoms; the PDOS of equivalent As atoms have been averaged. All PDOS have been normalized to 1. The As PDOS shows that the trough triple site causes band edge states. (d) PDOS (normalized to 1) of the Si and O atoms; the PDOS of equivalent Si and O atoms have been averaged. Similar to the As PDOS, band edge states also reside on the Si and O atoms.
FIGURE 1.11 (a) DOS (normalized to 1) for the clean surface and the surface containing the trough pyramid site. The undimerized As atom has been passivated with a H atom, therefore the states seen are only caused by the pyramid site. (b) Top-down model of the trough pyramid site with the atoms labeled that are seen in the PDOS. (c) PDOS (normalized to 1) of the relevant As atoms. The PDOS of equivalent As atoms have been averaged. The As PDOS shows that the trough triple site causes a state in the middle of the band gap. (d) PDOS (normalized to 1) of the Si and O atoms. The PDOS of equivalent Si and O atoms have been averaged. Similar to the As PDOS, the midgap state is also found to reside on the Si and O atoms.
1.8 Tables

TABLE 1.1 Summary of enthalpies of adsorption for row sites, with top-down models. The “ΔH (total)” column displays the enthalpy of reaction for the entire slab. The numbers in this column are divided by the number of SiO molecules per slab and the results are displayed in the “ΔH (per SiO)” column. It is necessary to calculate the “Corrected (per SiO)” values for structures that have an undimerized surface As atom in them. To calculate these corrected values, half of the stabilization energy for an As dimer is added to the ΔH (total) value and the resulting number is then divided by the number of SiO molecules in the slab.

<table>
<thead>
<tr>
<th>Row Sites</th>
<th>Top Down Cut Away View</th>
<th>$\Delta H_{ads}$ (Total)</th>
<th>$\Delta H_{ads}$ (Per SiO)</th>
<th>Corrected (Per SiO)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Single</td>
<td></td>
<td>-1.08 eV</td>
<td>-1.08 eV</td>
<td>N/A</td>
</tr>
<tr>
<td>Horizontal Double</td>
<td></td>
<td>-2.02 eV</td>
<td>-1.01 eV</td>
<td>N/A</td>
</tr>
<tr>
<td>Vertical Double</td>
<td></td>
<td>-2.10 eV</td>
<td>-1.05 eV</td>
<td>N/A</td>
</tr>
<tr>
<td>Compact Double</td>
<td></td>
<td>-1.15 eV</td>
<td>-0.58 eV</td>
<td>-0.87 eV</td>
</tr>
<tr>
<td>Triple</td>
<td></td>
<td>-1.28 eV</td>
<td>-0.43 eV</td>
<td>N/A</td>
</tr>
</tbody>
</table>

Legend: As, Ga, Si, O
TABLE 1.2 Summary of enthalpies of adsorption for trough sites, with top-down models. The “ΔH (total)” column displays the enthalpy of adsorption for the entire slab. The numbers in this column are divided by the number of SiO molecules per slab and the results are displayed in the “ΔH (per SiO)” column. It is necessary to calculate the “Corrected (per SiO)” values for structures that have an undimerized surface As atom in them. To calculate the corrected values, half of the stabilization energy for an As dimer is added to the ΔH (total) value and the resulting number is then divided by the number of SiO molecules in the slab.

<table>
<thead>
<tr>
<th>Trough Sites</th>
<th>Top Down Cut Away View</th>
<th>$\Delta H_{ads}$ (Total)</th>
<th>$\Delta H_{ads}$ (Per SiO)</th>
<th>Corrected (Per SiO)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Single</td>
<td></td>
<td>-1.32 eV</td>
<td>-1.32 eV</td>
<td>N/A</td>
</tr>
<tr>
<td>Vertical Double</td>
<td></td>
<td>-2.55 eV</td>
<td>-1.28 eV</td>
<td>N/A</td>
</tr>
<tr>
<td>Compact Double</td>
<td></td>
<td>-1.59 eV</td>
<td>-0.80 eV</td>
<td>-1.06 eV</td>
</tr>
<tr>
<td>Triple</td>
<td></td>
<td>-2.10 eV</td>
<td>-0.70 eV</td>
<td>N/A</td>
</tr>
<tr>
<td>Pyramid</td>
<td></td>
<td>-2.28 eV</td>
<td>-0.76 eV</td>
<td>-0.94 eV</td>
</tr>
</tbody>
</table>
1.9 Acknowledgments

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CHAPTER TWO

Electronic Properties of Adsorbates on GaAs(001)-c(2×8)/(2×4)

2.1 Abstract

A systematic experimental and theoretical study was performed to determine the causes of oxide-induced Fermi level pinning and unpinning on GaAs(001). Scanning tunneling spectroscopy (STS) and density functional theory (DFT) were used to study four different adsorbates’ (O₂, In₂O, Ga₂O, and SiO) bonding to the GaAs(001)-c(2×8)/(2×4) surface. The STS results revealed that out of the four adsorbates studied, only one left the Fermi level unpinned, Ga₂O. DFT calculations were used to elucidate the causes of the Fermi level pinning. Two distinct pinning mechanisms were identified: direct (adsorbate-induced states in the band gap region) and indirect pinning (generation of undimerized As atoms). For O₂ dissociative chemisorption onto GaAs(001)-c(2×8)/(2×4), the Fermi level pinning was only indirect, while direct Fermi level pinning was observed when In₂O was deposited on GaAs(001)-c(2×8)/(2×4). In the case of SiO on GaAs(001)-c(2×8)/(2×4), the Fermi level pinning was a combination of the two mechanisms.
2.2 Introduction

Over the last three decades multiple successful/unsuccessful attempts have been made to construct a GaAs-based metal-oxide-semiconductor field effect transistor (MOSFET) device. A GaAs-based MOSFET could potentially provide lower leakage current and lower standby power than current GaAs metal-semiconductor field effect transistors and high electron mobility transistors. In order to develop a GaAs-based MOSFET device with the best possible device characteristics, it is important to understand and characterize the oxide/GaAs interface at the molecular level. Having a molecular understanding of the interface facilitates the selection of the best oxide for a GaAs-based MOSFET device.

Previous studies using scanning tunneling microscopy (STM) performed by Kruse et al., Hale et al., and Winn et al. have detailed the bonding geometries of O$_2$, In$_2$O, Ga$_2$O, and SiO on the GaAs(001)-c(2×8)/(2×4) surfaces. Although complete STM studies of the bonding sites have been performed, only limited information is available on the electronic properties of these systems. Looking at a wide range of oxides allows more general conclusions to be drawn on the causes of Fermi level pinning of GaAs(001)-c(2×8)/(2×4).

Using the previously determined bonding sites, density functional theory (DFT) calculations were performed to help explain the experimental scanning tunneling spectroscopy (STS) results. The experimental STS studies showed that
Ga$_2$O left the Fermi level unpinned while O$_2$, In$_2$O, and SiO pinned the Fermi level. The Fermi level pinning was attributed to direct and/or indirect mechanisms.

2.3 Experimental and Computational Techniques

The experiments were performed in an UHV chamber with a base pressure of $3 \times 10^{-10}$ Torr. The chamber was equipped with low energy electron diffraction (LEED), and a Park Scientific VP STM with STS capabilities. As$_2$ capped $n$- and $p$-type GaAs wafers with Si and Be dopant concentrations of $2 \times 10^{17}$ cm$^{-3}$ were used for the Ga$_2$O and SiO experiments. For the O$_2$ and In$_2$O studies, wafers with dopant concentration of $2 \times 10^{16}$ cm$^{-3}$ were employed. The wafers were thermally decapped to the GaAs(001)-c(2×8)/(4×2) reconstruction by performing annealing cycles to 420ºC. Cycles were continued until no pressure rise was observed during the ramp (typically 20 cycles). Details of the decapping procedure have been discussed elsewhere.$^{68}$ The surface periodicity was then verified by employing both LEED and STM. Variable tip-sample separation differential conductance (dI/dV) measurements were taken to confirm that the clean surface was unpinned. Subsequently O$_2$, In$_2$O, Ga$_2$O, or SiO were deposited onto the surface. An effusion cell was used to deposit the In$_2$O, Ga$_2$O and SiO, while a UHV leak valve was employed for the O$_2$. Details of the deposition and dosing procedures are discussed elsewhere.$^{29,30,67,68}$ After deposition, the
electronic properties of the system were evaluated using STS. STS measurements were taken by employing the variable tip-sample separation method developed by Feenstra.\textsuperscript{37-39}

DFT calculations were performed using the Vienna \textit{ab initio} simulation package (VASP).\textsuperscript{51-54} The adsorbate/surface systems were modeled using an eight layer GaAs(001) slab that was bottom-terminated with H atoms having a $1.25e^-$ configuration. The bottom three layers of the slab, along with the H atoms were frozen in bulk position to preserve the bulk properties of the system. These calculations were performed using the Perdew-Burke-Ernzerhof (PBE)\textsuperscript{55} variation of the generalized gradient approximation. Atoms were modeled using projector augmented wave (PAW) potentials.\textsuperscript{56,69} The plane wave cut off energy was set to 400 eV and a $4 \times 4 \times 1$ Monkhorst-Pack\textsuperscript{58} k-point sampling scheme was used, which resulted in the generation of four irreducible k-points in the first Brillouin zone. The structures were considered fully relaxed when the interatomic forces were below 0.01 eV/Å. The calculations were assumed to be accurate within 0.10 eV; a more in-depth discussion on how the ±0.10 eV error value was reached is presented elsewhere.\textsuperscript{68}

\section*{2.4 Results and Discussion}
A. Bonding sites and enthalpies of adsorption

All of the systems of interest have their bonding geometries well documented in literature. Previous calculations performed on these systems could not be compared due to a lack of consistency in the computational methodologies. Figures 1 - 4 show top-down views of the experimentally observed sites for O, In₂O, Ga₂O, and SiO; in addition, the enthalpies of adsorption per molecule are displayed. The structures that incorporate an undimerized As atom in them (O single dimer displacements, SiO row compact double, SiO trough compact double, and SiO trough pyramid sites) have had their energies corrected by adding half the energy of an As dimer for every undimerized As atom in the calculation.

1. O₂ dissociative chemisorption

The DFT models of the two experimentally observed O sites are seen in Fig. 1. These sites include the single dimer displacement and the double dimer displacement sites. In these sites, either one or two O₂ molecules adsorb onto the surface and displace row As atoms that are adjacent to each other. This process generates excess As atoms on the surface. From the enthalpies of adsorption, it can be seen that the double dimer displacement [Fig. 1(b)] is only slightly more favorable (by 0.35 eV/O) than the single dimer displacement [Fig. 1(a)]. Kruse et al. experimentally showed that when GaAs(001)-c(2×8)/(2×4) is exposed to O₂, the surface contains a mixture of the two sites. One critical difference exists between the two sites; the single dimer
displacement causes the formation of two undimerized As atoms, while the double dimer displacement site does not.

2. In$_2$O chemisorption on rows and troughs

Hale et al.\textsuperscript{29} showed that when In$_2$O was deposited onto GaAs(001)-c(2×8)/(2×4) at 400ºC, even at low coverage, bonding sites formed in both the row and trough regions. At ~1 monolayer (ML) In$_2$O coverage, the average spacing between In$_2$O molecules was greater than 24 Å, revealing that the In$_2$O molecules had no affinity for clustering.

The enthalpies of adsorption of the seven In$_2$O bonding sites considered in this study are given in Fig. 2. Three of the sites are considered single sites because they only contain one In$_2$O molecule: row insertion [Fig. 2(a)], trough over dimer [Fig. 2(b)], and trough between dimer [Fig. 2(c)] sites. The insertion site occurs when an In$_2$O molecule inserts into a row As dimer. The trough sites occur when an In$_2$O molecule forms a bridge bond across the trough; the In$_2$O molecules can be positioned over the trough As dimers [trough over dimer site, Fig. 2(b)] or it can be positioned between two trough As dimers [trough between dimer site, Fig. 2(c)].

The sites remaining are combination sites and are formed by combining multiple single sites: row full coverage insertion [Fig. 2(d)], trough full coverage over dimers [Fig. 2(e)], trough triple [Fig. 2(f)], and complete coverage [Fig. 2(g)] sites. The adsorption energies of the combination sites show that clustering of In$_2$O molecules has no effect on the adsorption energy. Therefore, only three sites need to
be considered when discussing adsorption energies: row insertion, trough over dimer, and trough between dimer sites.

The adsorption energies of the three single sites show that the row insertion and trough over dimer sites are energetically degenerate within the error range of these calculations. These results are consistent with experimental findings that both row and trough sites form even at low coverage. The trough between dimer site is ~0.29 eV less stable than the row insertion and trough over dimer sites. Therefore, it is expected that the row insertion and trough over dimer sites will fill in before the trough between dimer sites start forming.

Hale et al. suggested that the In$_2$O molecules might be able to bond both O end up and down in the trough region. Multiple attempts were made to find stable structures for the trough over dimer and trough between dimer sites that had O atoms bonded downward into the trough. While no truly stable bonding geometries were found for these configurations, a weak metastable structure was found for the O down trough between dimer site. In order for the In$_2$O molecule to bond O down between trough dimers, it was necessary to have two other In$_2$O molecules bonded O end up over adjacent trough dimers, to prevent the In$_2$O molecule from flipping over in order to orient the O upwards. The adsorption energy for solely the “trapped” O down trough between dimer site was found to be only -0.57 eV. Therefore, it is not clear what role, if any, this site plays in the final bonding geometry picture.

The In$_2$O adsorption energies show that it is always energetically preferable to have an In$_2$O molecule bonded over a trough dimer than between trough dimers. This
difference in energy is most likely a result from interactions between the filled dangling bonds on the As trough dimers and the oxide molecule. The interaction is more severe in the between dimer site since the majority of the electron density in the filled dangling bonds is located in this position.

3. Ga$_2$O chemisorption on rows and troughs

Although one might predict that Ga$_2$O bonding on GaAs(001)-c(2×8)/(2×4) would be similar to In$_2$O bonding to GaAs(001)-c(2×8)/(2×4), there are actually major differences between these two isoelectronic systems. The STM images taken by Hale et al.\textsuperscript{30} of Ga$_2$O deposited onto GaAs(001)-c(2×8)/(2×4) showed that the initial bonding site for the Ga$_2$O molecules was to insert into the row As dimers. Unlike In$_2$O, no low coverage trough sites were ever experimentally observed.

The high coverage results for Ga$_2$O were also distinctly different than those for In$_2$O. At high coverage (~1 ML), the Ga$_2$O molecules were found to form parallel rows on the surface with the most common row spacing being ~8 Å. This result suggests that unlike In$_2$O, Ga$_2$O has an affinity for clustering. The ~8 Å, Ga$_2$O row spacing yielded a (2×2) surface periodicity. The typical separation between the As dimer rows on the GaAs(001)-c(2×8)/(2×4) surface is ~16 Å. Therefore, in order to form an ~8 Å row spacing, the surface would need to undergo a surface reconstruction. Experimentally, it was observed that as the concentration of Ga$_2$O on the surface increased, the number of steps also increased. It was assumed that this step formation generated the needed As atoms to allow for the (2×2) reconstruction to
form. Even though the majority of the In$_2$O molecules were found to have a row spacing of greater than 24 Å, a small number of In$_2$O molecules were found with a row spacing of ~8 Å. This suggests that small areas of the In$_2$O surface also might have undergone some rearrangement.$^{29}$

Calculations reveal that the row insertion site [Fig. 3(a)] is -1.87 eV exothermic, consistent with the low coverage experimental results. In addition, the adsorption energies of two trough sites were calculated for comparison with In$_2$O bonding sites. Although the trough sites were not observed with STM, the stability of the trough over dimer and trough between dimer sites (-1.06 and -0.69 eV, respectively) indicate that the trough filling mechanism is probably more complex than a simple As rearrangement.

Calculations were also attempted on a Ga$_2$O down trough sites but no stable/metastable sites were found. This was attributed to the fact that the Ga$_2$O molecules are slightly smaller than the In$_2$O molecules, which enables them to rotate into the energetically preferred position of O up, regardless of the surrounding environment.

In an effort to understand the energy discrepancy between the trough and row sites, an in-depth look must be taken at the fundamental bonding properties of the systems. On GaAs(001)-(2×4), when the Ga$_2$O inserts into the row, Ga-As bonds are created; conversely when Ga$_2$O bonds in the trough, Ga-Ga bonds are created. In covalent compounds, Ga-Ga bonds are ~1/2 as stable as Ga-As bonds.$^{70}$ The other major difference between the row and trough sites is that four bonds are created when
each row insertion site is formed and only two bonds are created when either of 
the two trough sites are formed.

Not only is it important to understand what bonding sites will be occupied, it is 
equally important to understand energetic differences between the In\(_2\)O and Ga\(_2\)O 
bonding sites on the GaAs(001)-c(2×8)/(2×4) surface. The Ga\(_2\)O trough site energies 
are comparable to the In\(_2\)O trough sites energies. However, the Ga\(_2\)O row insertion 
site is significantly more stable than the In\(_2\)O row insertion site (-1.87 eV vs. -1.18 eV, 
respectively). The difference in stability between the row insertion sites results from 
Ga-As and In-As bond strength differences. In order to estimate the approximate bond 
strength difference of Ga-As and In-As bonds, the enthalpies of reaction were 
calculated for the following two reactions using VASP.

\[
\begin{align*}
\text{Ga}_2\text{OAs}_4\text{H}_8 + 2\text{H}_2 & \rightarrow \text{Ga}_2\text{O} + 4\text{AsH}_3 \quad (1) \\
\text{In}_2\text{OAs}_4\text{H}_8 + 2\text{H}_2 & \rightarrow \text{In}_2\text{O} + 4\text{AsH}_3 \quad (2)
\end{align*}
\]

The difference in enthalpies of reaction is equal to four times the difference in bond 
energies between Ga-As and In-As bonds; this was calculated to be 0.57 eV. This 
value is comparable to the Ga\(_2\)O and In\(_2\)O insertion site energy differences (0.69 eV). 
Therefore, it can be concluded that the main difference between these two systems 
arises from the bond strengths.

4. SiO chemisorption on rows and troughs

Six bonding sites are experimentally observed at low coverage for SiO 
deposited on GaAs(001)-c(2×8)/(2×4) [Fig. 4]. These sites include row and trough
single [Figs. 4(a) and 4(b), respectively], row and trough compact double [Figs. 4(c) and 4(d), respectively], trough triple [Fig. 4(e)], and trough pyramid [Fig. 4(f)] sites. The row and trough single sites form when a SiO molecule inserts into an As-As dimer bond in either the row or trough. If an additional SiO molecule inserts between a single site and an adjacent dimer then the site is referred to as a row or trough compact double site. There are two more complex bonding geometries that are only found in the trough region: trough triple and trough pyramid sites. The trough triple site forms when two trough single sites bond in adjacent dimers and an additional SiO molecule bonds between the two occupied dimers. In order for a trough pyramid site to form, a trough compact double site forms, and subsequently, an additional SiO molecule bonds on top, forming a pyramid. A detailed investigation of these bonding sites along with a chemical potential plot showing that all of these geometries are viable bonding sites, depending on the SiO coverage, is presented elsewhere. The trough sites were found to be slightly more favorable than their row counterparts. This was attributed to stabilization received from the dangling bonds of the Ga atoms that protrude into the trough. In addition, the stabilization received from the dangling bonds of the Ga atoms allows the more complex sites (trough triple and trough pyramid sites) to form in the trough region.
B. Scanning tunneling spectroscopy and density of states measurements

Surface electronic measurements were taken of the different systems using STS. For all STS measurements, the Fermi level resides at 0 V. Figure 5(a) shows \( \frac{dI}{dV}/(I/V) \) vs. \( V \) measurements, which are proportional to the surface density of states (DOS), of the clean \( n \)- and \( p \)-type surfaces.\(^7\) The Fermi level resides near the conduction band for the clean, oxide-free \( n \)-type surface and resides near the valence band for the clean oxide-free \( p \)-type surface, typical of an unpinned surface.

DOS calculations were also performed on the clean surface [Fig. 5(b)], as well as the oxide covered surfaces. These calculations differ from STS measurements in two major ways. First, the computational slabs are not large enough to be doped; therefore, the computational slabs are intrinsic. Second, the position of the Fermi level within the band gap is somewhat arbitrary in DFT; therefore, in all the DFT calculations the DOS have been aligned using the deep level states. Regardless of these differences, if the calculated DOS shows adsorbate induced states within the band gap region, it can be reasonably concluded that the adsorbate would cause the experimental surface to be pinned.

1. \( \text{O}_2 \) chemisorbate electronic structure

Figure 6(a) shows a STS measurement of \( n \)-type sample after \(~900 \text{ L}\) exposure to \( \text{O}_2 \). The conduction band is not observed for this \( n \)-type sample due to the low dopant concentration of the wafer, which prohibits complete inversion from being
obtained during the STS measurement. The STS measurement reveals that the bands have bent causing the Fermi level to be located midgap (~0.7 V from the valence band edge); this is typical of a pinned sample. Although no \textit{p}-type STS spectra are presented in this paper, other groups have verified that exposing O\textsubscript{2} to GaAs pins the Fermi level.\textsuperscript{12,13}

To deduce the cause of the Fermi level pinning seen experimentally, DOS and projected density of states (PDOS) calculations were performed. Figure 6(b) presents the calculated DOS for a surface containing two O atoms that have replaced two As atoms, and a surface containing four O atoms that have replaced four As atoms. The DOS of the clean surface is also displayed for comparison. The plots reveal that states are only generated in the band gap region when two O atoms replace two As atoms. To further investigate which atoms contribute to the states in the DOS, PDOS calculations were performed. PDOS calculations for the surface As atoms are seen in Fig. 6(c). The PDOS reveals that the major contributors to the midgap states are the undimerized As atoms. This also rationalizes why no states are observed in the band gap region when four O atoms replace four As atoms, because no undimerized As atoms are generated. This suggests that the properties of the O atoms do not directly cause Fermi level pinning on the GaAs(001)-\textit{c}(2×8)/(2×4) surface; instead, the pinning is most likely due to the generation of undimerized As atoms. Therefore, the pinning mechanism is considered to be indirect. Previous reports incorrectly attributed the pinning to a direct mechanism but this was due to inferior or incorrect computational methods.\textsuperscript{30}
On real (experimental) surfaces, the undimerized As atoms may be able to redimerize, thereby eliminating the midgap As states, if two criteria are met. First, the activation barrier must be low enough to allow for the reconstruction of the row, in order to facilitate the redimerization of the As atoms. Second, there must be another undimerized As atom in the same row to terminate the process with a complete dimer. Although it might be possible to meet both of these constraints, the second criteria becomes harder to fulfill on smaller terraces. If these criteria cannot be met, and undimerized As atoms remain on the surface, the Fermi level is expected to be pinned.

H atoms can be used to (computationally) passivate these undimerized As atoms in order to verify that they are the only cause of O induced states. Figure 6(d) displays the DOS for a surface containing two O atoms and two undimerized As atoms, and a surface containing two O atoms with the undimerized As atoms passivated with H atoms. The plot clearly shows that the H passivation suppresses the states in the band gap region, yielding a DOS that is similar to the clean unpinned surface. This result indicates that it is the resultant dangling bonds on the undimerized As atoms that causes the observed Fermi level pinning. This result also indicates that H passivation can be used for any system that has undimerized As atoms; once the H atoms have been used to passivate the undimerized As atoms, any states left in the band gap region are a direct result of the adsorbate bonding with the surface.

2. In$_2$O chemisorbate electronic structure
STS results of In$_2$O on GaAs(001)-c(2×8)/(2×4) are presented in Fig. 7(a). Although the $n$-type sample has the same STS spectra as the unpinned surface, the $p$-type sample clearly shows that the In$_2$O deposited on GaAs(001)-c(2×8)/(2×4) causes the Fermi level to be pinned near the conduction band edge.

The DOS of the In$_2$O single sites (row insertion, trough over dimer, and trough between dimer) in Fig. 7(b) shows that none of these sites induce states in the band gap region. Although the single sites do not cause state formation in the band gap, all of the combination sites (row full coverage insertion, trough full coverage over dimers, trough triple, and complete coverage) induce states into the band gap region, as shown in Fig. 7(c). As the coverage on the row increases from the row insertion site to the full coverage insertion site, state formation is seen in the band gap region. Similarly, as the trough coverage increases form the single trough sites to the trough full coverage over dimer site, and finally to the trough triple site the state density in the band gap region also increases. These results suggest that the higher the In$_2$O coverage, the greater the state formation in the band gap. This was further substantiated by the DOS for the experimentally observed high coverage site (complete coverage in which every available site is filled), which has the highest state formation in the band gap region of all the sites. A PDOS analysis revealed that the pinning states were delocalized and existed throughout the top four layers of the slab.

Hale et al. reported that room temperature deposition resulted in In$_2$O molecules inserting into missing As row dimers (defect sites). Calculations were performed on this geometry and the site was shown to only be marginally stable (-0.33
eV). The DOS revealed that these empty dimer sites generated states in the band gap. However, it is not believed that this site plays a major role in the Fermi level pinning since the concentration of these sites is very low.

In$_2$O pinning is distinct from pinning by the other oxides (O$_2$ and SiO) on GaAs(001)-c(2×8)/(2×4) because In$_2$O experimentally pins the Fermi level near the conduction band edge while the other oxides experimentally pin the Fermi level midgap. Although states generated in the band gap region are distinctly different depending on whether multiple row or multiple trough sites caused the formation, both types of states can be evaluated to understand why In$_2$O pins the Fermi level near the conduction band. Multiple row insertion sites induce states that start at the valence band edge and extend toward the conduction band, residing in over half of the band gap region. Analysis of the Kohn-Sham orbital occupancies indicates that these are filled states. These results imply that the Fermi level should indeed be pinned near the conduction band edged inside the reduced band gap. The states that are generated when the coverage increases and multiple trough sites are forced to form in close proximity to each other are located at both the valence and conduction band edges. Although it is clear that these states play a role in the Fermi level pinning, it is difficult to conclude exactly where the Fermi level should reside as a result.

3. Ga$_2$O chemisorbate electronic structure

Experimental and calculated electronic structures of Ga$_2$O on GaAs(001)-c(2×8)/(2×4) are displayed in Fig. 8. STS measurements [Fig. 8(a)] show that the
Fermi level resides close to the conduction band for $n$-type samples and close to the valence band for $p$-type samples, revealing that Ga$_2$O leaves the GaAs(001)-c(2×8)/(2×4) surface unpinned. These findings were further substantiated by the fact that the calculated DOS [Fig. 8(b)] for the insertion site had no states in the band gap region. The DOS for the trough over dimer and trough between dimer sites are also displayed in Fig. 8(b), for comparison with the In$_2$O system. Although these sites are not explicitly seen experimentally, the DOS reveals that both the Ga$_2$O trough between dimer and trough over dimer sites also have no states in the band gap region.

The Ga$_2$O insertion site leaves the Fermi level unpinned because the insertion site does not trigger any chemical event which causes Fermi level pinning. In contrast to O$_2$ chemisorption on the GaAs(001)-c(2×8)/(2×4) surface, the Ga$_2$O insertion site does not cause the generation of undimerized As atoms nor does it cause the generation of excess As atoms. In addition, when a Ga$_2$O molecule bonds on the row, the filled dangling bonds on the row As atoms are preserved, and no extra dangling bonds are introduced.

The electronic effects of increased coverage were also computationally explored for Ga$_2$O on GaAs(001)-(2×4). Similar to In$_2$O all of the higher coverage Ga$_2$O sites pinned the Fermi level. However, the simulated high coverage sites for Ga$_2$O do not represent the experimental surface since they do not result in a (2×2) surface reconstruction. Therefore, these results are not relevant to the examination of the electronic properties of Ga$_2$O on GaAs(001)-c(2×8)/(2×4).
Calculations were also performed for a Ga$_2$O molecule inserting into a missing As row dimer. Similar to the In$_2$O case this site was also found to induce states into the band gap region. In addition, the bonding geometry was found to be significantly more stable for Ga$_2$O than for In$_2$O (-0.42 eV more stable). Therefore, since Ga$_2$O was experimentally shown to leave the Fermi level unpinned the number of defect sites must be small enough to not play a major role in the electronic properties of the system.

4. SiO chemisorbate electronic structure

STS of SiO on GaAs(001)-c(2×8)/(2×4) is presented in Fig. 9(a). The STS results reveal that SiO deposition on GaAs experimentally pins the Fermi level at midgap. The calculated DOS for the row and trough adsorption sites are seen in Figs. 9(b) and 9(c), respectively. The DOS have H atoms passivating any undimerized As atoms that were generated by the bonding sites, leaving only the states directly induced by the SiO molecules. These DOS show that only two of the six geometries (trough triple and pyramid sites) directly induce states in the band gap region. These results are consistent with the experimental findings. In addition, the compact double sites and the pyramid site generate undimerized As atoms, which most likely play an indirect role in the Fermi level pinning.

PDOS analysis was performed on the trough triple [Fig. 9(d)] and trough pyramid [Fig. 9(e)] sites to deduce the causes of state formation in the band gap region for SiO bonded to the GaAs(001)-c(2×8)/(2×4) surface. The PDOS from the trough
triple site [Fig. 9(d)] shows that the states observed near the conduction band edge in the DOS reside on the surface As, Si, and O atoms. A Bader style atomic charge analysis\textsuperscript{62} revealed that the likely cause of the band gap states in the trough triple site was from a local buildup of charge on multiple adjacent As atoms. Similar to the PDOS of the trough triple site, the trough pyramid site PDOS [Fig. 9(e)] reveals that the band gap states also reside on the surface As, Si, and O atoms. The band gap states were attributed to the generation of partially filled dangling bonds on the bottom Si atoms of the trough pyramid site. A more in-depth study of the SiO/GaAs(001)-c(2×8)/(2×4) surface is presented elsewhere.\textsuperscript{68}

\textbf{2.5 Conclusion}

Experimental results revealed that out of the four adsorbates studies (O\textsubscript{2}, In\textsubscript{2}O, Ga\textsubscript{2}O, and SiO) only one, Ga\textsubscript{2}O, left the Fermi level unpinned when it bonded to GaAs(001)-c(2×8)/(2×4). DFT simulations were used to explain the different pinning mechanisms for other adsorbates. The mechanisms can be broken down into two general categories: direct and indirect. Direct Fermi level pinning results when the bonding between the adsorbate and the surface directly induces states into the band gap region. In comparison, indirect Fermi level pinning occurs when states are induced in the band gap region because of secondary effects, such as the generation of undimerized As atoms. Since indirect pinning is not caused by the properties of the
adsorbates themselves, it may be possible to create unpinned surfaces using H
passivation or even a multilayer of oxide. Adsorbates that cause Fermi level pinning on GaAs(001)-c(2×8)/(2×4) can either exhibit one of the pinning mechanisms [O (indirect) and In₂O (direct)] or they can exhibit both of the mechanisms (SiO). In addition, the close correlation between experiment and theory in this study suggests that DFT can be used on other III-V semiconductor systems to predict oxide pinning and unpinning.
2.6 Figures

FIGURE 2.1 Top-down views of the lowest energy structures of $O_2$ bonded to the GaAs(001)-c(2×8)/(2×4) surface: (a) single dimer displacement, and (b) double dimer displacement. The adsorption energy per oxide molecule is displayed below each structure. The energy denoted with "*" has been corrected to include half the As dimerization energy for each undimerized As atom.
FIGURE 2.2 Top-down views of the lowest energy structures of In$_2$O bonded to the GaAs(001)-c(2×8)/(2×4) surface: (a) row insertion, (b) trough over dimer, (c) trough between dimer, (d) row full coverage insertion, (e) trough full coverage over dimer, (f) trough triple, and (g) complete coverage. The adsorption energy per oxide molecule is displayed below each structures.
FIGURE 2.3 Top-down views of the lowest energy structures of Ga$_2$O bonded to the GaAs(001)-c(2×8)/(2×4) surface: (a) row insertion, (b) trough over dimer, and (c) trough between dimer. The adsorption energy per oxide molecule is displayed below each structure.
FIGURE 2.4 Top-down views of the lowest energy structures of SiO bonded to the GaAs(001)-c(2×8)/(2×4) surface: (a) row single, (b) row compact double, (c) trough single, (d) trough compact double, (e) trough triple, and (f) trough pyramid. The adsorption energy per oxide molecule is displayed below each structure. The energies denoted with “*” have been corrected to include half the As dimerization energy for each undimerized As atom.
FIGURE 2.5 (a) STS measurements of the clean $n$-type (black solid line) and $p$-type (grey dashed line) GaAs(001)-c(2×8)/(2×4) surface. (b) Calculated DOS for the clean surface.
FIGURE 2.6 (a) STS measurement of O$_2$ adsorbed onto $n$-type GaAs(001)-$c$(2×8)/(2×4). (b) DOS calculations of O$_2$ sites: clean surface (thick bold line), single dimer displacement (●), and double dimer displacement (▲). (c) PDOS calculations showing the average of the surface As atoms that are dimerized (●) vs. the average of the surface As atoms that are not dimerized (▲). (d) DOS calculations of the unpassivated single dimer displacement (●) and the single dimer displacement with the undimerized As atoms passivated with H atoms (thick bold line).
FIGURE 2.7 (a) STS measurements of In$_2$O adsorbed onto $n$-type (black line) and $p$-type (gray dashed line) GaAs(001)-c(2×8)/(2×4). (b) DOS calculations of In$_2$O sites: clean surface (black line), insertion (●), over dimer (▲), and between dimer (+). (c) DOS calculations of combination sites: row full coverage insertion (●), trough full coverage over dimers (▲), trough triple (+), and complete coverage (×).
FIGURE 2.8 (a) STS measurements of Ga$_2$O adsorbed onto $n$-type (black line) and $p$-type (gray dashed line) GaAs(001)-$c(2\times8)/(2\times4)$. (b) DOS calculations of Ga$_2$O sites: clean surface (thick bold line), row insertion (●), trough over dimer (▲), and trough between dimer (+) sites.
FIGURE 2.9 (a) STS measurements of SiO adsorbed onto $n$-type (black bold line) and $p$-type (grey dashed line) GaAs(001)-c(2×8)/(2×4). (b) DOS calculations of the row SiO sites: clean surface (thick bold line), row single (●), and row compact double (▲). (c) DOS of the trough SiO sites: clean surface (thick bold line), trough single (●), trough compact double (▲), trough triple (+), and trough pyramid (♦). (d) PDOS calculations for the trough triple sites, atoms which PDOS have been plotted for are labeled in the ball-and-stick diagram in the upper right hand corner of the plot, the thick black line is a PDOS of a trough As dimer on the clean surface for comparison. (e) PDOS calculations for the trough pyramid sites, atoms which PDOS have been plotted for are labeled in the ball-and-stick diagram in the upper right hand corner of the plot, the thick black line is a PDOS of a trough As dimer on the clean surface and the dashed line is the As atom with the H bonded to it.
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CHAPTER THREE

Definitive Identification of the InAs(001)-c(8×2)/(4×2) Reconstruction

3.1 Abstract

InAs(001) is well documented to have a (4×2) reconstruction, however, the details of the reconstruction are still under debate. Atomically resolved filled and empty state scanning tunneling microscopy (STM) images of the InAs(001)-c(8×2)/(4×2) surface reveal that the reconstruction is made up of single atom rows that run in the [110] direction which are separated by ~17 Å. In addition, atomically resolved STM images show that the row structure is most likely comprised of undimerized atoms. Cl₂ was deposited onto the surface (which has been shown to preferentially react with III atoms on III-V semiconductors) to confirm that the rows were in fact comprised of In atoms. The experimental results suggest that the most probable structure for InAs(001)-c(8×2)/(4×2) is the undimerized β3(4×2) reconstruction also known as the β3(4×2)' reconstruction. Density functional theory (DFT) STM simulations were used to confirm the experimental findings.
3.2 Introduction

Due to InAs’s high electron mobility (30,000 cm²Vs⁻¹) it is a potential channel material candidate for a III-V metal oxide semiconductor field effect transistor (MOSFET) device. An atomic understanding of the oxide semiconductor interface can greatly enhance the electronic properties of the device. Unfortunately, even the clean InAs(001) surface has not been well documented in literature.

Although it is well documented that InAs(001) has a (4×2) surface reconstruction, there is still disagreement about the exact atomic placement of the surface atoms. Since InAs and GaAs have similar chemical properties, it might be assumed that the (4×2) reconstruction of the two semiconductors would be the same. However, scanning tunneling microscopy (STM) images of the two surfaces differ dramatically. Despite the differences in STM images between InAs(001)-(4×2) and GaAs(001)-(4×2), some groups still propose that the InAs structure is the same ζ(4×2) reconstruction that has been well documented for GaAs. Other groups have proposed different (4×2) structures that include the α(4×2), β2(4×2), and β3(4×2). These structures along with four other possible (4×2) reconstructions [α2(4×2), α3(4×2), β(4×2), and S(4×2)] are seen in Fig. 1. Although numerous papers have attempted to determine the InAs(001)-(4×2) reconstruction, the majority of the papers focused either on experimental determination or computational determination of the surface but do not employ both techniques.
Experimental and computational studies were employed for this paper to help determine the InAs(001)-c(8×2)/(4×2) reconstruction. Detailed STM images of the clean surface allowed for the elimination of many of the possible (4×2) structures. In addition, the chemical makeup of the row atoms was determined by depositing Cl\textsubscript{2} onto the surface and observing the Cl chemisorption sites. Density functional theory (DFT) calculations were also performed to confirm the experimental findings. The most probable InAs(001)-c(8×2)/(4×2) reconstruction was identified as the undimerized β3(4×2) structure.

### 3.3 Experimental and Computational Techniques

Experiments were performed in two UHV chamber that were both equipped with low energy electron diffractometer (LEED), Auger electron spectrometer (AES), and different types of STMs. The majority of the STM experiments were performed on a Park Scientific VP STM. An Omicron LT STM was also employed for some of the experiments; images taken with the Omicron system are labeled within the text of the paper. As capped InAs(001) wafers were thermally decapped to the InAs(001)-c(8×2)/(4×2) surface by performing ramping cycles to ~450ºC. Details of the decapping procedure are discussed elsewhere.\textsuperscript{68} LEED was used to verify the surface periodicity, after which the samples were transferred into the STM for analysis. This included obtaining atomically resolved filled and empty state STM images.
After the clean surface had been confirmed, Cl$_2$ was deposited onto the surface. This was achieved by opening a leak valve on the chamber and allowing 2% Cl$_2$ in N$_2$ to flow into the chamber until the pressure in the chamber reached $1 \times 10^{-8}$ Torr. STM movies were made by continually taking STM images during the 30 min Cl deposition, which allowed for the monitoring of reacted Cl sites.

DFT calculations were used to confirm the experimental results. Plane wave (periodic boundary) calculations were performed using the Vienna Ab-initio simulation package (VASP) code.$^{51-54}$ For the current study, a nine atomic layer slab was used which was terminated by H atoms having a charge of 1.25 e$^-$. In order to preserve the bulk like properties of the system, the bottom three layers of the slab, along with the H atoms, were frozen in bulk position. In addition, thirteen layers of vacuum were used to keep interactions with the top and bottom of the slabs to a minimum. Calculations were performed using the Perdew-Burke-Ernzerhof (PBE)$^{55}$ variant of the general gradient approximation. Atoms were modeled using projector augmented wave (PAW)$^{56,57}$ potentials as supplied by VASP. A $2 \times 4 \times 1$ Monkhorst-Pack k-point sampling scheme was employed which resulted in the generation of 4 irreducible k-points in the first Brillouin zone. The plane wave cut off energy was set to 500 eV. The relaxation criteria were set to terminate the calculations once the forces were below 0.01 eV/Å. However, this level of accuracy was never reached. The forces dropped until the highest force was 0.06 eV/Å and subsequently the forces stabilized. It is possible that the inability of the slab to fully relax stems from the large overlap between the conduction and valence bands preventing the true ground state from being reached.
3.4 Experimental Results and Discussion

A. Clean InAs(001)-c(8×2)/(4×2) surface

A large scale (450 × 450 Å²) STM image of the clean surface is seen in Fig. 2(a). The image reveals bright long straight rows that run in the [110] direction. The rows are separated by ~17 Å and have a row thickness of ~7 Å. The effects of sample bias on the STM images were explored by taking filled [Fig. 2(b)] and empty [Fig. 2(c)] state images, in the same region. The bias dependent images show, that the trough structure is more readily resolved in empty state images, than in filled state images. These STM results are consistent with images published in literature.⁷⁷,⁷⁸

The information gleaned from the STM images can help eliminate some of the possible (4×2) structures. First, the row thickness can help determine how many dimers reside in the row. If the rows were made up of double dimers, then the row thickness should be comparable to the row thickness of the $\beta_2(2\times4)$ reconstruction which has a two dimer row structure. The $\beta_2(2\times4)$ reconstruction has rows that are ~9 Å thick: since the experimentally observed rows on the (4×2) structure are only ~7 Å wide this suggest that the (4×2) structure has a single dimer structure. This eliminates $\alpha(4\times2)$, $\beta(4\times2)$, $\beta_2(4\times2)$, and the $\zeta(4\times2)$ reconstructions as possible structures for InAs(001)-c(8×2)/(4×2). Second, the rows in the STM images are straight and do not zigzag. Therefore, the reconstruction cannot have multiple structures of
approximately the same energy. For example, Fig. 3(a) and 3(b) show energetically degenerate structures for the $\alpha_{2}(4\times2)$ reconstruction. Since the two structures are energetically degenerate, the experimental surface would contain a distribution of the two sites, Fig. 3(c). This would cause the rows in STM images to appear to zigzag. Since this is not observed in the InAs(001)-c(8×2)/(4×2) STM images, reconstructions $\alpha_{3}(4\times2)$, $\alpha_{2}(4\times2)$, and $\alpha_{3}(4\times2)$ can be eliminated as possible structures. Lastly it has been well documented that the trough region of InAs(001)-c(8×2)/(4×2) is better resolved in empty state imaging.\textsuperscript{77} This suggests that the dimers in the trough are made up of In dimers. This eliminates $\alpha_{3}(4\times2)$, $\alpha_{3}(4\times2)$, $\beta_{3}(4\times2)$, and $\zeta_{3}(4\times2)$ as possible reconstruction candidates.

From the STM images, all but two of the structures can be eliminated as the possible InAs(001)-(4×2) structure. The two remaining structures are the $\beta_{3}(4\times2)$ and S(4×2) reconstructions. These structures differ in one important way; the S(4×2) reconstruction has As dimers on the row while the $\beta_{3}(4\times2)$ reconstruction has In dimers on the row. Although the $\beta_{3}(4\times2)$ and S(4×2) reconstructions have different row structures their trough structures are identical; both trough structures are comprised of two parallel In dimers.

B. Defects on the InAs(001)-c(8×2)/(4×2) surface

For clean semiconductor surfaces, defect sites usually consist of missing atoms as opposed to contaminants, therefore, they can be used to verify structural models. If
a commonly found defect cannot be explained using the given structural model the structural model is most likely flawed. Figure 4(a) and 4(b) show filled and empty state images of the InAs(001)-c(8×2)/(4×2) surface respectively; red circles have been drawn around six of the same type of trough defect sites. This type of defect site changes dramatically depending on the applied sample voltage. In filled state images, the defect appears as two bright spots that are separated by ~12.5 Å. In empty state images, the defect site images as a depression and causes the trough rungs to be separated by ~12.5 Å instead of ~8.5 Å. Kendrick et al. also observed the trough defect site on InAs(001)-c(8×2)/(4×2) but they never identified the cause of the defect.77

The defect site is most likely two missing trough In atoms, which results in the trough structure shifting its reconstruction by one half of a unit cell, (Fig. 5). When the trough shifts by a half of unit cell, it causes the surface to shift between the (4×2) and the c(8×2) reconstructions. In order to determine if this is the correct defect site, it is helpful to imagine how this site should appear in both filled and empty state images. The missing In atoms, leave two As atoms that are only bonded to two In atoms. Therefore, these As atoms should both have two filled or partially filled dangling bonds. Although it is unclear exactly how this charge redistributes, if some of the charge was relocated into the dangling bonds of the nearby In atoms it would cause these atoms to image slightly brighter in filled state images. In empty state images this defect would be expected to shift the trough rung spacing from ~8.5 Å to ~12.5 Å.
Since the defect sites can be explained within the \( \beta_3(4\times2) \) and \( S(4\times2) \) models, each of these is a viable contender for the InAs(001)-c\((8\times2)/(4\times2)\) reconstruction.

C. **Atomically resolved row structure**

Both the \( \beta_3 \) and the S models have the same trough structure, therefore, the trough defect site did not allow for the elimination of either of these two structures. In an effort to identify the row structure, atomic resolved images of the row were taken with an Omicron LT STM. Figure 6 shows an STM image of the InAs(001)-c\((8\times2)/(4\times2)\) surface along with a line scan down the length of a row. The line scan reveals that the row is comprised of individual atoms that are separated by ~4.3 Å.

The atomically resolved STM image along with the line scan reveals that the \( S(4\times2) \) model cannot be the correct reconstruction for InAs(001)-c\((8\times2)/(4\times2)\). The \( S(4\times2) \) model has dimers that run perpendicular to the row which would be expected to image wider in the [\( \bar{1}10 \)] than the [110] which is in conflict with the experiments. In addition, if the \( S(4\times2) \) model was correct, one would expect a commonly seen defect site to be a missing surface As atom. This would cause the row to narrow whenever a defect site was present. However, this has never been seen experimentally.

The atomically resolved image and line scan also reveal problems with the \( \beta_3(4\times2) \) model. The \( \beta_3(4\times2) \) model has dimers that run in [110] direction. These dimers should be separated by ~8.5 Å. The line scan reveals however, that along the
row the spacing is ~4.3 Å. This suggests that instead of having dimers on the row, the rows are comprised of undimerized atoms. Figure 7 shows a ball-and-stick diagram of the undimerized β3(4×2) structure (also referred to as the β3(4×2)' reconstruction).

D. Cl adsorbed onto InAs(001)-c(8×2)/(4×2)

Identifying the row atoms as In or As atoms can help further confirm the (4×2) reconstruction. However, atomic composition is difficult to identify in STM images; in order to identify the atomic composition of the surface, other techniques need to be employed. Cl has been shown to preferentially react with III atom in III-V semiconductors. This is impart due to the fact that Cl is extremely electronegative and is inclined to bond to atoms which are good electron donors.

STM images of the clean InAs(001)-c(8×2)/(4×2) surface and the same area of the surface after Cl₂ deposition are seen in Fig. 8(a) and 8(b) respectively. After Cl₂ deposition, the STM image reveals depressions on the rows. These depressions are the reacted Cl sites. AES was used to further confirm that Cl was deposited on the surface. Since the Cl atoms adsorbed onto the rows, it is reasonable to assume that the rows are comprised of In atoms on InAs(001)-c(8×2)/(4×2). As previously mentioned, it is believed that the trough is also comprised of In dimers. However, no reacted sites were ever observed in the trough region. This is most likely due to poor tip resolution. These findings further suggest that the β3(4×2)' structure is the most likely reconstruction for InAs(001)-c(8×2)/(4×2).
3.5 Computational Results and Discussion

The experimental results strongly suggest that the InAs(001)-c(8×2)/(4×2) reconstruction is the β3(4×2)' structure. In order to further confirm these findings, DFT was used to simulate both the β3(4×2) and the β3(4×2)' reconstructions. Top-down views of the two slabs are seen in Fig. 9. Each compositional slab consists of two unit cells.

Tersoff and Hamann STM simulations were calculated in order to compare the DFT results with the experimental findings. Filled and empty state STM simulations of the β3(4×2) and the β3(4×2)' along with experimental images are presented in Fig. 10(a) and 10(b). Filled state STM simulations of both reconstructions show that the prominent features are caused by electrons tunneling out of the filled dangling bonds of the second layer As atoms. Subtle differences exist between the filled state images of the two structures. In the β3(4×2) STM simulation, In dimers are position in the center of four As atoms. These In dimers cause a slight rise in electron density with ~8.5 Å periodicity. This rise in electron density has never been seen experimentally. The row In atoms of the β3(4×2)' reconstruction are aligned with the As atoms in the [110] direction, eliminating the increases in electron density that are calculated for the β3(4×2) structure. In empty state STM simulations, the majority of the electron density is a result of electrons tunneling into the empty dangling bonds of the surface.
In atoms. The $\beta 3(4\times2)$ structure has In dimers and the $\beta 3(4\times2)'$ structure has undimerized In atoms, therefore, the spacing in row charge maximums are calculated to be $\sim 8.5$ Å for $\beta 3(4\times2)$ and $\sim 4.3$ Å for $\beta 3(4\times2)'$. Experimentally only charge maximums with $\sim 4.3$ Å periodicity have been observed. Therefore, the $\beta 3(4\times2)'$ STM simulations are a closer fit to experimental findings.

The experimental data suggests that the InAs(001)-c(8×2)/(4×2) reconstruction is the $\beta 3(4\times2)'$ structure. This structure is unusual because it contains undimerized surface atoms. In order to deduce why it is preferable to have undimerized row In atoms, the bonding geometries within both the $\beta 3(4\times2)$ and $\beta 3(4\times2)'$ structures have been studied.

If the surface atoms are dimerized then the In atoms in the dimer should be sp$^2$ hybridized, which should have As-In-As ideal bond angles of 120º [Fig 11(a)]. However, the DFT computation shows this bond angle is $\sim 142$º consistent with a large amount of strain on the rows. In addition, the As atoms directly bonded to these In dimers have a partially filled dangling bond. To calculate the number of electrons in the dangling bond, it is assumed that atoms on the surface give the same number of electrons to bonds that they do in the bulk (similar to the electron counting model). Therefore, when an As atom bonds to an In atom, the As atom contributes 5/4 of an electron to the bond. If this assumption is employed, dangling bonds on the surface As atoms contain 5/4 e$^-$. It is energetically unfavorable to have a radical on the surface thereby making the reconstruction less favorable.
If the surface In atoms are undimerized, then the first layer In atoms should be sp hybridized. DFT computations show the As-In-As bond angle is 179º which is essentially the ideal sp hybridized bond angles [Fig. 11(b)]. The distribution of surface electrons also changes significantly for the \(\beta_3(4\times2)'\) reconstruction. Having undimerized In atoms allows the In atoms to form double bonds to the surface As atoms. Electrons that were in the partially filled dangling bonds on the surface As atoms in the \(\beta_3(4\times2)\) structure, relocate to form the double bond thereby making the system more energetically favorable.

A closer look can be taken at bond length to confirm that first layer In atoms are sp\(^2\) hybridized in the \(\beta_3(4\times2)\) reconstruction and sp hybridized in the \(\beta_3(4\times2)'\) reconstruction. The first layer In atoms in the \(\beta_3(4\times2)\) reconstruction should form single bonds to the second layer As atoms, conversely, the first layers In atoms should form double bonds with the second layer As atoms for the \(\beta_3(4\times2)'\) reconstruction. Double bonds are shorter than single bonds, therefore, comparing the dimerized and undimerized bond lengths can confirm the hybridization of the first layer In atoms. The As-In bond length in the \(\beta_3(4\times2)\) structure is 2.64 Å while the As-In bond length in the \(\beta_3(4\times2)'\) structure is 2.52 Å showing that a double bond has most likely formed for the \(\beta_3(4\times2)'\) reconstruction while a single bond has formed for the \(\beta_3(4\times2)\) reconstruction.

Although only the \(\beta_3(4\times2)'\) reconstruction is observed experimentally, this geometry is degenerate with the \(\beta_3(4\times2)\) structure (0.04 eV energy difference between the two structures). This difference in energy is very small considering it is spread out
between the 12 row In atoms and the As atoms to which they are bonded. In addition, the 0.04 eV difference might have a significant error. DFT has been well documented to do a poor job of calculating electronic structures of narrow band gap semiconductors such as InAs. The electronic structure of the InAs slabs show a significant overlap between the conduction band and the valence band. This overlap most likely causes deviations between the calculated ground state and the actual ground state of the system. This suggests that the atomic placements are slightly askew, leading to higher than normal errors in the energy. These errors may be significant enough to widen the energy gap between the two structures.

### 3.6 Conclusion

Filled and empty state STM images helped identify the InAs(001)-c(8×2)/(4×2) reconstruction as the $\beta 3(4\times2)'$ structure. This reconstruction was found to significantly different from other surfaces because the row In atoms formed double bonds. These double bonds were able to form due to In’s ability to be sp hybridized. DFT STM simulations were also found to be in good agreement with the $\beta 3(4\times2)'$ model.
3.7 Figures

FIGURE 3.1 Possible structures for the InAs(001)-(4×2) reconstruction. The red boxes denote the unit cells of the systems.
FIGURE 3.2 (a) 450 × 450 Å² STM image (Vs = -2 V, It = 0.5 nA) of the InAs(001)-c(8×2)/(4×2) surface. (b) 150 × 150 Å² filled state image (Vs = -2 V, It = 0.2 nA) of the InAs(001)-c(8×2)/(4×2) surface reconstruction (c) 150 × 150 Å² empty state image (Vs = 2 V, It = 0.2 nA) of the same area of InAs(001)-c(8×2)/(4×2).
FIGURE 3.3 (a) Ball-and-stick diagram of the α2(4×2) reconstruction. (b) Ball-and-stick diagram of an energetically degenerate structure of the α2(4×2) reconstruction. (c) Ball-and-stick diagram of what an experimental α2(4×2) surface would look like.
FIGURE 3.4 (a) 225 × 225 Å² filled state STM image (\(V_s = -2\) V, \(I_t = 0.2\) nA) of the InAs(001)-c(8×2)/(4×2) surface with most common row defect circled in red. (b) 225 × 225 Å² empty state STM image of the same area (\(V_s = 2\) V, \(I_t = 0.2\) nA) of the InAs(001)-c(8×2)/(4×2) surface with same defects circled in red.
FIGURE 3.5 Ball-and-stick diagram of the proposed defect site on InAs(001)-\(\beta\)3(4\(\times\)2).
FIGURE 3.6 120 × 120 Å² atomically resolved STM image (V_s = -2.2 V, I_t = 0.05 nA) and line scan corresponding to the black line on the STM image showing individual atoms separated by ~4.3 Å.
FIGURE 3.7 Ball-and-stick diagrams of the $\beta$3(4×2) and the $\beta$3(4×2)$'$ reconstructions.
FIGURE 3.8 (a) 425 × 425 Å² STM image ($V_s = -1$ V, $I_t = 0.2$ nA) of the clean InAs(001)-c(8×2)/(4×2) surface. (b) 425 × 425 Å² STM image ($V_s = -1$ V, $I_t = 0.2$ nA) of the same location after 30 min deposition of Cl₂.
FIGURE 3.9 Top-down views of the $\beta 3(4\times2)$ and $\beta 3(4\times2)'$ computational slabs.
FIGURE 3.10 (a) Filled state STM simulations of the $\beta 3(4\times2)$ (top left) and the $\beta 3(4\times2)'$ (top right) reconstructions along with a filled state STM image ($V_s = -2$ V) (bottom). (b) Empty state STM simulation of the $\beta 3(4\times2)$ (top left) and the $\beta 3(4\times2)'$ (top right) reconstructions along with a empty state STM image ($V_s = 2$ V) (bottom).
FIGURE 3.11 Ideal and computational bonding angles for the (a) $\beta 3(4\times2)$ and (b) $\beta 3(4\times2)'$ reconstructions along with In-As bond lengths.
3.8 Acknowledgments

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CHAPTER FOUR

Electronic Properties of Adsorbates on
$\text{In}_{0.37}\text{Ga}_{0.63}\text{As}(001)-(2\times4)$

4.1 Abstract

The molecular and electronic structures of $\text{In}_2\text{O}$ and $\text{Ga}_2\text{O}$ bonding to the As-rich $\text{In}_{0.37}\text{Ga}_{0.63}\text{As}(001)-(2\times4)$ surface were investigated using density functional theory (DFT) calculations. The DFT calculations revealed that the bonding enthalpies of $\text{In}_2\text{O}$ and $\text{Ga}_2\text{O}$ on $\text{In}_{0.37}\text{Ga}_{0.63}\text{As}(001)-(2\times4)$ were almost identical to the bonding enthalpies of $\text{Ga}_2\text{O}$ and $\text{In}_2\text{O}$ on $\text{GaAs}(001)-(2\times4)$. Although the density of states (DOS) calculations for oxides bonding onto $\text{In}_{0.37}\text{Ga}_{0.63}\text{As}(001)-(2\times4)$ and $\text{GaAs}(001)-(2\times4)$ are very similar, subtle differences are observed. In both cases the Fermi level pinning became more severe as the number of molecules in close proximity was increased. However, it took more oxide molecules bonded in close proximity before Fermi level pinning was seen for InGaAs than for GaAs. The alloy structure had only minor effects on the bonding geometry and the electronic structure of the adsorbates. Instead, the lower density of band edge states for oxides bonding on the $\text{In}_{0.37}\text{Ga}_{0.63}\text{As}(001)-(2\times4)$ vs. $\text{GaAs}(001)-(2\times4)$ is due to band gap size differences.
4.2 Introduction

InGaAs is a promising material for long wavelength optical communication devices. Several groups have attempted to construct an InGaAs metal oxide semiconductor field effect transistor (MOSFET) device. Currently, the InGaAs devices have substrates that are either GaAs or InP. Increasing the In content raises the mobility of the alloy, but lattice matched alloys are limited to ~30% In content for very thin layers of InGaAs (~100 Å) on GaAs. While higher In content alloys can be grown on InP, InGaAs/GaAs is of technical interest due to the availability of large GaAs substrates and the ability to grow GaAs on Ge or GOI (Ge on insulator) wafers. Multiple studies have investigated oxides deposited on InGaAs in order to ascertain which oxide induces the least amount of states in the band gap region. These oxides include Ga$_2$O$_3$(Gd$_2$O$_3$), Al$_2$O$_3$, and the thermal oxidation of AlAs. Although groups have been able to demonstrate both working depletion and enhancement mode MOSFET devices, the electronic properties of these devices could be improved with an atomic understanding of the oxide/InGaAs interface.

In spite of the technological importance of InGaAs(001), only recently has work been performed to understand and characterize the surface at the atomic level. In order to characterize the clean surface, several groups have performed scanning tunneling microscopy (STM) studies to identify the different surface reconstructions of InGaAs(001). Although there are still disagreements about the exact surface
reconstructions, most groups agree that there are at least \((2\times4)\) and \((n\times3)\) surface reconstructions.\(^{82-84}\)

Very few computational papers have been published on InGaAs(001),\(^{85-90}\) and no papers address oxide bonding on the InGaAs(001)-(2×4) surface. In this manuscript, DFT calculations will be presented of the clean \(\text{In}_{0.37}\text{Ga}_{0.64}\text{As}(001)-(2\times4)\) surface along with calculations predicting the bonding geometries of \(\text{In}_2\text{O}\) and \(\text{Ga}_2\text{O}\) bonding with the clean surface. The 37\% In content was chosen because it is close to the maximum In content for very thin InGaAs layers on GaAs.

### 4.3 Computational Techniques

\(\text{In}_{0.37}\text{Ga}_{0.63}\text{As}(001)-(2\times4)\) was modeled using plane-wave (periodic boundary) DFT calculations. The calculations were performed using the Vienna \textit{ab initio} simulation package (VASP).\(^{51-54}\) Slabs consisted of eight atomic layers with the bottom layer being terminated with H atoms. In order to preserve the bulk like properties of the system, the bottom three layers of the slab, along with the H atoms, were frozen in bulk position. Eleven layers of vacuum were used to avoid interactions between the top and the bottom of the slabs. The calculations were performed using the PW91 variant of the general gradient approximation.\(^{55}\) Atoms were modeled using ultrasoft pseudopotentials as supplied by VASP.\(^{69,91}\) A \(4\times2\times1\) Monkhorst-Pack\(^{58}\) \(k\)-point sampling scheme was employed which resulted in the generation of four
irreducible k-points in the first Brillouin zone. The plane wave cut off energy was set to 475 eV, and the slab was considered fully relaxed when the forces were less than 0.03 eV/Å. The error in these calculations is assumed to be ±0.1 eV. A detailed discussion of how the ±0.1eV error was reached is presented elsewhere.\textsuperscript{68}

4.4 Results and Discussion

A. Clean In\textsubscript{0.37}Ga\textsubscript{0.63}As(001)-(2×4) surface

DFT calculations have been performed on numerous III-V semiconductors. However, when modeling a compound III-V semiconductor, such as InGaAs, the procedure is slightly more complicated due to variability in the locations of the In and Ga atoms. Figure 1(a) shows a ball and stick diagram of the clean InGaAs(001)-(2×4) surface. As atoms are depicted as orange circles and In or Ga atoms are depicted as black circles. An In concentration of 37\% was used for this study resulting in a slab that contained 11 In atoms and 19 Ga atoms.

The main complication in deciding the placement of the In and Ga atoms is that although the placements can be random within the slab, once the slab is tiled in all directions, there is long-range order. In an effort to verify that long-range order will not effect the calculations, four different slabs were constructed with random placements of the Ga and In atoms [Fig. 1(b)-1(e)]. The four slabs had energies of -280.23, -280.06, -280.75, and -289.48 eV. The span in energies results from
differences in surface energy of the structures along with bulk energy differences most likely due to strain. The molecular beam epitaxially grown samples are expected to have a random placement of In and Ga atoms in the bulk with slightly higher In concentrations at the surface.\textsuperscript{92}

Although the differences in total energy between the four slabs are not substantial, it is also important to verify that the In and Ga placements do not effect the electronic properties of the system. Figure 2 shows the density of states (DOS) of the four different geometries. From the plot, it can be seen that the electronic properties of the slabs remain the same regardless of the placements of the In or the Ga atoms. Therefore, only one bonding geometry was chosen [Fig. 1(b)] for subsequent calculations upon the bonding of In\textsubscript{2}O and Ga\textsubscript{2}O molecules to the In\textsubscript{0.37}Ga\textsubscript{0.63}As(001)-(2×4) surface.

\section*{B. In\textsubscript{2}O and Ga\textsubscript{2}O bonding to In\textsubscript{0.37}Ga\textsubscript{0.63}As(001)-(2×4)}

The In\textsubscript{2}O and Ga\textsubscript{2}O bonding sites along with the enthalpies of adsorption are presented in Fig. 3. Winn \textit{et al.}\textsuperscript{93} did a similar study of In\textsubscript{2}O and Ga\textsubscript{2}O bonding to the GaAs(001)-(2×4) surface; a summary of their findings along with the findings in the current paper are seen in Table 1. Although the computational methods vary slightly, the overall trends between the two systems can be compared.

Calculations were performed on three different bonding sites for both In\textsubscript{2}O and Ga\textsubscript{2}O. The row bonding site forms when an oxide molecule inserts into the As row
dimers; this is referred to as a “row insertion” site. In addition to the row site, two
different trough sites were also examined. The first trough site is the “trough over
dimer” site and forms when an oxide molecule bonds to the group III atom at the
trough edge making a bridge site over an As trough dimer. The second trough site is a
“trough between dimer” site and forms when an oxide molecule bonds to the group III
molecule at the trough edge making a bridge site between the As trough dimers.

The enthalpies of adsorption for the In$_2$O bonding sites on In$_{0.37}$Ga$_{0.63}$As(001)-(2×4) are presented in Fig. 3(a). The row insertion site and the trough over dimer site
are essentially degenerate in energy. Therefore, it is reasonable to assume that In$_2$O
molecules will occupy both the row insertion sites and the trough over dimer sites,
even at low coverage.

For In$_2$O/In$_{0.37}$Ga$_{0.63}$As(001)-(2×4), the significant difference in adsorption
energies between the two trough sites is most likely a result of dissimilar bonding
environments. An In$_2$O molecule that bonds between the trough As dimers has an
unfavorable interaction with the filled dangling bonds on the trough As dimers while
the oxide molecule that bonds over the trough As dimer has no unfavorable
interactions with the filled dangling bonds on the trough As dimers. This results in the
trough between dimer site being less energetically favorable than the trough over
dimer site.

Figure 3(b) gives the enthalpies of adsorption for the Ga$_2$O bonding sites on
In$_{0.37}$Ga$_{0.63}$As(001)-(2×4). Although one might expect Ga$_2$O and In$_2$O adsorption
energies to be nearly the same, they have major differences. The Ga$_2$O row insertion
site is significantly more stable than the In$_2$O row insertion site (-1.86 eV/Ga$_2$O and -1.12 eV/In$_2$O, respectively). Resulting in the Ga$_2$O row insertion site being significantly more stable than any of the other Ga$_2$O bonding geometries on In$_{0.37}$Ga$_{0.63}$As(001)-(2×4). Therefore, at low coverage only the Ga$_2$O row insertion sites are expected to form on In$_{0.37}$Ga$_{0.63}$As(001)-(2×4). The difference in Ga$_2$O and In$_2$O stability on GaAs(001)-(2×4) results from the stronger Ga-As bonds forming a more stable row insertion site than the weaker In-As.$^93$ Since the same type of bonds are formed when In$_2$O and Ga$_2$O bond to In$_{0.37}$Ga$_{0.63}$As(001)-(2×4), the energy difference for the row insertion sites on In$_{0.37}$Ga$_{0.63}$As(001)-(2×4) can again be ascribed to the Ga-As and In-As bond strength differences.

The Ga$_2$O/In$_{0.37}$Ga$_{0.63}$As(001)-(2×4) enthalpies of adsorption clearly show that the most favorable bonding geometry is the row insertion site. The differences in adsorption energies between the Ga$_2$O/In$_{0.37}$Ga$_{0.63}$As(001)-(2×4) bonding geometries are attributed to three causes. First, Ga-As bonds are stronger than Ga-Ga bonds, causing the row site to be more stable than the trough sites.$^93$ Second, the row site forms four new bonds while the trough sites only form two, which causes the row site to be more stable than the trough sites. Third, as with In$_2$O bonding to In$_{0.37}$Ga$_{0.63}$As(001)-(2×4), unfavorable interaction exists between the filled dangling bonds on the trough As dimer and the trough between dimer site.

Although no experiments have been performed to verify the In$_2$O or the Ga$_2$O bonding sites on In$_{0.37}$Ga$_{0.63}$As(001)-c(2×8)/(2×4), the computations can be compared to the experimentally found binding sites for In$_2$O and Ga$_2$O on GaAs(001)-
Experimental results reveal that In\textsubscript{2}O bonds to both the row and the trough regions on GaAs(001)-c(2×8)/(2×4) at low coverage. Conversely, experiments show that Ga\textsubscript{2}O only bonds to the row on GaAs(001)-c(2×8)/(2×4) at low coverage. These results are consistent with the computational findings for In\textsubscript{2}O and Ga\textsubscript{2}O on In\textsubscript{0.37}Ga\textsubscript{0.63}As(001)-(2×4).

C. Density of states and projected density of states calculations

Previous DOS calculations for In\textsubscript{2}O and Ga\textsubscript{2}O on GaAs(001)-(2×4) were performed on a double slab (two unit cells put together).\textsuperscript{93} This allowed for both half coverage of sites (every other site filled in) and full coverage of sites (every site filled in). In the current study, only one unit cell was simulated, therefore, only full coverage results were obtained. Previous studies found that none of the half coverage sites on GaAs(001)-(2×4) pinned the Fermi level.\textsuperscript{93} However, as the coverage increased, states began to form in the band gap region for both In\textsubscript{2}O and Ga\textsubscript{2}O bonded to GaAs(001)-(2×4). However, none of the high coverage calculated sites were ever seen experimentally for Ga\textsubscript{2}O on GaAs(001)-(2×4).

Figure 4(a) shows the DOS for the three different In\textsubscript{2}O bonding sites. Of the three sites, only one site introduces states into the band gap (row insertion site). As the concentration of In\textsubscript{2}O molecules in close proximity to each other increases to complete trough coverage (every possible trough site filled in which utilizes both
types of trough sites), the density of states induced in the band gap region also increases [Fig. 4(b)].

The DOS results for In$_2$O on In$_0.37$Ga$_0.63$As(001)-(2×4) can be compared to the DOS results for In$_2$O on GaAs(001)-(2×4). For In$_2$O on GaAs(001)-(2×4), the full coverage insertion and full coverage over dimer sites both had states within the band gap region with the largest density of states in the band gap region being generated by the full coverage row insertion site. Conversely, when In$_2$O bonds onto In$_0.37$Ga$_0.63$As(001)-(2×4), the only site that generates states in the band gap region is the row insertion site. These calculations suggest that Fermi level pinning is less severe for In$_2$O bonding to In$_0.37$Ga$_0.63$As(001)-(2×4) than for In$_2$O bonding to GaAs(001)-(2×4). When In$_2$O bonds to either In$_0.37$Ga$_0.63$As(001)-(2×4) or GaAs(001)-(2×4), it induces states near the band edges. Since InGaAs has a smaller band gap than GaAs, these In$_2$O induced states most likely reside outside the band gap region for InGaAs while they reside inside the band gap region for GaAs. As the In$_2$O coverage increases the number of states also increases causing the states to be observed in the band gap region for InGaAs.

Figure 5(a) shows the DOS for the three different Ga$_2$O bonding geometries on In$_0.37$Ga$_0.63$As(001)-(2×4). The only site that causes state formation in the band gap region is the trough between dimer site. The calculated Ga$_2$O/ In$_0.37$Ga$_0.63$As(001)-(2×4) sites are comparable to full coverage sites for Ga$_2$O/GaAs(001)-(2×4) which have pinned Fermi levels for both the row full coverage insertion and the trough full coverage over dimer sites.
If the Ga$_2$O concentration is increased to complete trough coverage by bonding Ga$_2$O molecules in every available trough site (filling in all between and over dimer sites) on In$_{0.37}$Ga$_{0.63}$As(001)-(2×4), the Fermi level pinning worsens [Fig. 5(b)]. These results suggest that similar to GaAs the Fermi level pinning gets more severe as additional Ga$_2$O molecules bond in close proximity to each other. However, for InGaAs a greater Ga$_2$O coverage is needed compared to GaAs before Fermi level pinning is observed. InGaAs has a smaller band gap than GaAs, therefore, some of the states that are seen when Ga$_2$O bonds with GaAs(001)-(2×4) are located outside the band gap region for InGaAs.

### 4.5 Conclusion

DFT calculations were performed to simulate In$_2$O and Ga$_2$O bonding to In$_{0.37}$Ga$_{0.63}$As(001)-(2×4). Although the adsorption energies are nearly the same for In$_2$O and Ga$_2$O adsorbing onto In$_{0.37}$Ga$_{0.63}$As(001)-(2×4) or GaAs(001)-(2×4), the electronic properties differ slightly. In both cases, increasing the density of oxide molecules increases the density of states in the band gap. However, the number of states in the band gap region was smaller for the oxides on In$_{0.37}$Ga$_{0.63}$As(001)-(2×4) than on GaAs(001)-(2×4). In$_2$O and Ga$_2$O induced states are mainly located at the band edges. The InGaAs band gap is smaller than the GaAs band gap causing a significant amount of the pinning states to be located outside the band gap region for
InGaAs. This suggests that in general, forming an unpinned oxide interface on narrow band gap semiconductors may be easier than on wide band gap semiconductors. It also suggests that the presence of disorder in the placement of atoms in ternary semiconductors has little effect on the atomic and electronic structure of the interface when the atoms are chemically similar (Ga and In as opposed to Ga and Al).
4.6 Figures

FIGURE 4.1 (a) Ball-and-stick diagram of the clean InGaAs(001)-(2×4) surface. (b) Side and top-down views of geometry 1. (c) Side and top-down views of geometry 2. (d) Side and top-down views of geometry 3. (e) Side and top-down views of geometry 4.
FIGURE 4.2 DOS of four different slabs with random In placements: geometry 1(●), geometry 2 (▲), geometry 3(+), and geometry 4(♦). All of the DOS line up, therefore, the In placement does not effect the electronic properties of the slab.
FIGURE 4.3 Top-down views of the (a) In$_2$O and (b) Ga$_2$O bonding sites on In$_{0.37}$Ga$_{0.63}$As(001)-(2×4).
FIGURE 4.4 (a) DOS of the single In$_2$O bonding sites on In$_{0.37}$Ga$_{0.63}$As(001)-(2×4): clean surface (black solid line), row insertion site (●), trough over dimer (▲), and trough between dimer (+) sites. (b) DOS of the clean surface (black solid line) and a surface with the trough completely filled in with In$_2$O molecules (every over and between dimer site occupied) (●).
FIGURE 4.5 (a) DOS of the single Ga$_2$O bonding sites on In$_{0.37}$Ga$_{0.63}$As(001)-(2×4): clean surface (black solid line), row insertion (●), trough over dimer (▲), and trough between dimer (+) sites. (b) DOS of the clean surface (black solid line) and a surface with the trough completely filled in with Ga$_2$O (every over and between dimer site occupied) (●).
### 4.7 Tables

**TABLE 4.1** Summary of the findings for In$_2$O and Ga$_2$O bonding to the GaAs(001)-(2×4) and In$_{0.37}$Ga$_{0.63}$As(001)-(2×4).

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</tr>
</tbody>
</table>

Grayed box denote pinned structures
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