ATOMIC DIFFUSION AND INTERFACE ELECTRONIC STRUCTURE OF III-V HETEROJUNCTIONS AND THEIR DEPENDENCE ON EPITAXIAL GROWTH TRANSITIONS AND ANNEALING

DISSERTATION

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Achieving the abrupt interfaces necessary for III-V based devices presents a challenge in situations where both Group-III and Group-V sources are switched during an interface growth transition. Group-V exchange reactions and Group-III chamber memory effects are reported for a number of III-V systems. These phenomena, along with atomic rearrangements associated with cross-diffusion, can introduce interface-localized defects that adversely affect device performance. Additionally, the need to vary growth temperature with epilayer composition, as well as surface interactions during the early stages of interface growth, leads to differences between layer A grown on B versus layer B grown on A. The trend of device miniaturization and, correspondingly, high operating temperatures, makes understanding these interfacial interactions increasingly important.

In order to clarify the role of chemical interactions and atomic rearrangement in determining interface electronic structure, cathodoluminescence spectroscopy (CLS), secondary ion mass spectrometry (SIMS), and a number of complementary techniques are used to perform measurements of representative, lattice-matched double heterostructures (DH) involving growth transitions with both cation and anion source-switching. The role of source-switching sequence and post-growth annealing in determining interface structure is quantified in InGaAs/InP, AlInP/GaAs, and InGaP/GaAs. I present evidence demonstrating that interface and bulk electronic
structure depends sensitively on growth conditions, anneal temperature, and the resulting diffusion, thereby correlating cross-diffusion with defect emission and highlighting the asymmetric chemical and electronic differences due to growth sequence. Overall, these results demonstrate that interfacial cross-diffusion and exchange reactions have a significant impact on the electronic structure of lattice-matched III-V heterostructures.
Dedicated to my parents, Mark and Linda Smith
This research could not have been completed without the mentoring and insight provided by my advisor, Dr. Leonard Brillson. I have benefited greatly from his knowledge and enthusiasm while working in his labs.

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LIST OF ABBREVIATIONS AND SYMBOLS

2DEG – 2-Dimensional Electron Gas
AES – Auger Electron Spectroscopy
BJT – Bipolar Junction Transistor
CASINO – monte CArlo Simulation of electroN trajectory In sOlids
CLS – CathodoLuminescence Spectroscopy
DH – Double Heterostructure
EBD – Electron Beam Deposition
EBIC – Electron Beam Induced Current
$E_{\text{act}}$ – Activation Energy
$E_g$ – Energy (Band) Gap
EHP – Electron Hole Pair
EMNLab – Electronic Materials and Nanostructures Laboratory
$E_{\text{vac}}$ – Vacuum Level Energy
GSMBE – Gas Source Molecular Beam Epitaxy
HEMT – High Electron Mobility Transistor
HPGE – High Purity Germanium dEtector
IILD – Impurity Induced Layer Disordering
IR – Infrared

xx
LHe – Liquid Helium
LRO – Long-range Ordering
MBE – Molecular Beam Epitaxy
MESFET – Metal Semiconductor Field Effect Transistor
OSU – Ohio State University
pHEMT – Pseudomorphic High Electron Mobility Transistor
PL – PhotoLuminescence
PMT – PhotoMultiplier Tube
RMS – Root Mean Square
SED – Secondary Electron Detector
SEM – Scanning Electron Microscopy
SET – Secondary Electron Threshold
SIMS – Secondary Ion Mass Spectrometry
SSMBE – Solid Source Molecular Beam Epitaxy
UHV – Ultra High Vacuum
XCLS – cross sectional CathodoLuminescence Spectroscopy
XSTM – cross sectional Scanning Tunneling Microscopy
$\Delta E_c$ – Conduction Band Offset
$\Delta E_v$ – Valence Band Offset
$\Phi$ - Work Function
$\chi$ - Electron Affinity
CHAPTER 1

INTRODUCTION AND BACKGROUND

1.1 InGaAs on InP

1.1.1 Basic Properties and Importance of the InGaAs/InP System

Semiconductor devices based on an InP platform are the focus of intense research owing to their applications in optoelectronics and high-speed electronics. The In$_x$Ga$_{1-x}$As/InP system is particularly useful as an optoelectronic material because the band-gap $E_g$ ($1.55 \ \mu m$) of the lattice-matched composition ($x = 0.53$) corresponds to a well in the absorption spectrum of silica-based fibers. Alloying InGaAs with P allows for greater flexibility in designing lattice-matched optoelectronics including infrared (IR) photodetectors and light-emitters, and an additional 1.30 $\mu m$ window in the silica fiber absorption spectrum can be accessed.\(^1\)

Electronically, InP-based transistors have a number of advantages over their GaAs-based counterparts in high speed, microwave, and millimeter-wave systems. The GaAs metal-semiconductor field effect transistor (MESFET) is an industry standard; however, its operational frequency is limited to applications running at $< 30$ GHz.\(^2\) The GaAs high electron mobility transistor (HEMT) is capable of higher speeds by utilizing a higher band-gap, highly doped AlGaAs layer, from which electrons can drop into an
undoped GaAs channel. A two-dimensional electron gas (2DEG) at the AlGaAs/GaAs interface, where electrons avoid impurity scattering, allows for high operating speeds in these devices. To further increase confinement at this interface it is desirable to increase the conduction band-offset ($\Delta E_c$). This is accomplished by adding a strained In$_{1-x}$Ga$_x$As channel layer between GaAs and AlGaAs (pseudomorphic HEMT, or pHEMT). To prevent the relaxation of this layer and the subsequent formation of dislocations, In incorporation and channel thickness are restricted by the lattice mismatch between epitaxial layers. Using an InP substrate circumvents this requirement since In$_{0.53}$Ga$_{0.47}$As is lattice-matched to InP, as is Al$_{0.48}$In$_{0.52}$As. Figure 1.1 shows an InP-based HEMT and the location of the 2DEG.

Figure 1.1: InP-based HEMT structure showing the location of the 2DEG. These devices exhibit a high electron mobility by confining carrier movement to an undoped, InGaAs-based channel.

For added performance, the In mole fraction in the channel layer can be increased, leading to a strained-layer pHEMT. The high InAs electron mobility, coupled with a
high $\Delta E_c$ at the InGaAs/AlInAs interface (which leads to a high 2DEG density), gives considerable speed advantages to these devices. InGaAs/InP based pHEMTs demonstrating $f_T > 600$ GHz and $f_{max} > 300$ GHz are reported, and InP-based devices operating in the THz regime may be possible.\textsuperscript{3,4} InP is also of interest for heterojunction bipolar transistors (HBTs). InP-based HBTs have a lower turn on voltage, power dissipation, and better $1/f$ noise performance characteristics than their GaAs-based counterparts. Table 1.1 shows important 300 K material properties of the III-V binary semiconductors relevant to this thesis, along with Si for use as a reference.

<table>
<thead>
<tr>
<th>Property</th>
<th>Si</th>
<th>InP</th>
<th>GaAs</th>
<th>AlP</th>
<th>GaP</th>
<th>InAs</th>
</tr>
</thead>
<tbody>
<tr>
<td>Band-gap $E_g$ (eV)</td>
<td>1.12</td>
<td>1.351</td>
<td>1.424</td>
<td>2.45*</td>
<td>2.27*</td>
<td>0.411</td>
</tr>
<tr>
<td>Lattice Constant (Å)</td>
<td>5.431</td>
<td>5.869</td>
<td>5.653</td>
<td>5.464</td>
<td>5.451</td>
<td>6.058</td>
</tr>
<tr>
<td>Electron Mobility $\mu$ (cm(^2)/V/s)</td>
<td>1350</td>
<td>5370</td>
<td>9200</td>
<td>60</td>
<td>160</td>
<td>33000</td>
</tr>
<tr>
<td>Thermal conductivity $\xi$ (W/cm K)</td>
<td>1.5</td>
<td>0.7</td>
<td>0.54</td>
<td>0.9</td>
<td>1.1</td>
<td>0.26</td>
</tr>
<tr>
<td>Dielectric constant $\varepsilon$</td>
<td>11.8</td>
<td>12.56</td>
<td>13.18</td>
<td>9.8</td>
<td>11.11</td>
<td>15.15</td>
</tr>
<tr>
<td>Electron Affinity (eV)</td>
<td>4.05</td>
<td>4.40</td>
<td>4.07</td>
<td>4.0</td>
<td>4.90</td>
<td></td>
</tr>
</tbody>
</table>

Table 1.1: Comparison of 300 K material properties for relevant III-V binary semiconductors.\textsuperscript{1} An asterisk denotes an indirect band-gap. Si is included as a reference.
1.1.2 Growth and Interdiffusion at InGaAs/InP Junctions

Despite its commercial importance and an abundance of research, there remains controversy on the physical and electronic microstructure of the InGaAs/InP interface. This is due in part to the wide variety of growth methods and procedures commonly used. InGaAs/InP heterointerface growth remains difficult because both cation and anion sources switch during growth transitions. To maintain the high anion to cation beam pressure ratio necessary for two-dimensional growth, an anion “soak” (i.e., anion exposure without growth) is typically used during growth transitions. This soak allows the new anion pressure to equilibrate in the chamber prior to the growth of subsequent layers, thereby ensuring a Group-V terminated surface.

Owing to the complex interactions between atomic species, an anion soak during interface source-switching has consequences for interface microstructure. During an As soak at the InGaAs-on-InP interface, the replacement of several monolayers of P by As due to an exchange reaction is widely reported.\textsuperscript{5-8} Activation energies for this As-P exchange reaction are reported to be in the 1.2-1.7 eV range.\textsuperscript{9,10} Subsequent exposure to P eliminates As and restores the InP surface; however, immediately starting InGaAs growth after As exposure results in the trapping of As atoms in the recently grown InP layer.\textsuperscript{11} At T $> 500^\circ\text{C}$ it is reported that, after an initial 10s replacement period where 7.5 Å of InAs is formed, As diffuses into InP via a Frank-Turnbull\textsuperscript{12} mechanism to fill vacancies in the InP bulk. This As in-diffusion can lead to interfacial roughening and island formation due to the 3.2% lattice mismatch between InAs and InP.\textsuperscript{10,13-15} Perhaps due to the wide variety of growth methods used, as well as the need to tailor growth parameters to individual growth systems, the composition and width of the
InGaAs-on-InP transition layer is disputed. Using cross-sectional scanning tunneling microscopy (XSTM), an 0.5 nm InAs$_{0.65}$P$_{0.35}$ interfacial layer is observed in MOVPE-grown material.$^{16,17}$ Others observe up to 95% As replacement of P over 5.5 monolayers at $T = 450^\circ\text{C}$,$^{18}$ and intermixing on scales as large as 20 nm, owing partially to chamber memory effects (residual atoms in the growth chamber incorporating during new layer growth), is documented.$^{19}$ Additionally, Raman spectroscopy studies report evidence of P incorporation in the InGaAs lattice at growth or anneal temperatures above 640$^0\text{C}$.$^{20,21}$ Diffusion in InGaAs/GaAs DHs is generally thought to occur via an interstitial-based mechanism on the Group-III sublattice, and a vacancy-based mechanism on the Group-V sublattice.$^{22}$

Table 1.2 lists the heat of formation $\Delta H_f$ for binary III-V compounds relevant to this thesis.

<table>
<thead>
<tr>
<th>Bond</th>
<th>$\Delta H_f$ (kJ/mol)</th>
<th>$\Delta H_f$ (eV/molecule)</th>
</tr>
</thead>
<tbody>
<tr>
<td>In-P</td>
<td>-75.3</td>
<td>-0.780</td>
</tr>
<tr>
<td>Ga-P</td>
<td>-107.5</td>
<td>-1.114</td>
</tr>
<tr>
<td>Al-P</td>
<td>-164.4</td>
<td>-1.703</td>
</tr>
<tr>
<td>Ga-As</td>
<td>-74.1</td>
<td>-0.768</td>
</tr>
<tr>
<td>Al-As</td>
<td>-116.3</td>
<td>-1.205</td>
</tr>
<tr>
<td>In-As</td>
<td>-57.5</td>
<td>-0.598</td>
</tr>
</tbody>
</table>

Table 1.2: Heat of formation $\Delta H_f$ for binary III-V compounds relevant to this thesis. Values are given in kJ/mol and eV/molecule.$^{23}$
Due to the similar $\Delta H_f$ of the In-P and Ga-As bonds (-0.780 versus -0.768 eV/molecule respectively), along with the relatively weak In-As bond (-0.598 eV/molecule), it might be expected that a similar replacement reaction occurs early in InP-on-InGaAs interface growth. The replacement of As by P is observed in GaAs with P exposure at $T < 900^0{\text{C}}$.24 In GaAs, P in-diffusion is thought to occur via a Frank-Turnbull or kick-out mechanism depending on the temperature of the diffusion. At the InP-on-InGaAs interface, P replacement of As is reported to produce an $\text{In}_{0.53}\text{Ga}_{0.47}\text{As}_x\text{P}_{1-x}$ interfacial layer with $x$ from 0.2-0.8, the composition being largely dependent on the source-switching sequence.16,17 Similarly to the InGaAs-on-InP interface, roughening is often observed with P-beam exposure on the InGaAs surface prior to InP growth.26,27 A different source-switching sequence that includes the deposition of a mixed monolayer of Group-III atoms precludes As-P exchange, demonstrating the critical dependence of interface structure on source-switching sequence.28

Such differences in interface microstructure are expected to affect interface-related optical and electrical properties. Indeed, an extended interface soak results in a broadened near-band-edge (NBE) cathodoluminescence emission at InGaAs/InP interfaces and, correspondingly, is known to alter the performance of single quantum well (SQW) structures.14,29 Electrically, an extended anion soak is reported to increase carrier lifetimes measured by photoconductive decay (PCD) due to an As-defect related persistent photoconductivity (PPC).30 HEMT channel mobility is a function of interface abruptness and is also known to be affected by an extended anion soak.31
1.2 AlInP and InGaP on GaAs

1.2.1 Basic Properties and Importance of AlInP and InGaP/GaAs Systems

Al\textsubscript{x}In\textsubscript{1-x}P, In\textsubscript{1-x}Ga\textsubscript{x}P, and the alloy (Al\textsubscript{y}Ga\textsubscript{1-y})\textsubscript{x}In\textsubscript{1-x}P, are of considerable interest for both optoelectronic and electronic devices. This system spans the band-gap range 1.34-3.57 eV and the endpoint (y = 0 or 1) ternaries can be grown lattice-matched to GaAs. These lattice-matched compositions are \(x = 0.52\) and 0.51 for Al\textsubscript{x}In\textsubscript{1-x}P and In\textsubscript{1-x}Ga\textsubscript{x}P respectively (AlInP and InGaP denote these compositions through the remainder of this thesis). The lattice-matched compositions have \(\Gamma\)-point band-gaps of 2.57 (AlInP) and 2.05 eV (InGaP) at 4 K. The 300 K structures of the In\textsubscript{1-x}Ga\textsubscript{x}P \(\Gamma\) and \(X\)-bands are given by:

\[
E_{\text{g}\Gamma}(\text{In}_{1-x}\text{Ga}_xP) = 1.32 + 1.14x + 0.34x^2 \\
E_{\text{g}X}(\text{In}_{1-x}\text{Ga}_xP) = 2.00 + 0.26x
\]  

(1.1)

The indirect crossover point based on Equation (1.1) is \(x \approx 0.62\). This agrees favorably with independent absorption measurements indicating a crossover point of \(x = 0.61\).\textsuperscript{33} The lattice-matched composition (\(x = 0.51\)) therefore exhibits a direct-gap that can be measured by standard optical methods and utilized for optical devices.

InGaP has a number of desirable properties for modern semiconductor-based devices and is a promising alternative to AlGaAs/GaAs structures, where Al is highly susceptible to the incorporation of deep donors (DX centers) which act as traps. A low interface recombination velocity with GaAs,\textsuperscript{34} a low impact ionization coefficient,\textsuperscript{35} and the availability of selective etchants versus GaAs, make InGaP attractive for devices.
InGaP is also of interest for HBTs due to its low $\Delta E_c$ with GaAs and, correspondingly, a high emitter injection efficiency (i.e., low reverse injection of holes) which leads to high current gain.\textsuperscript{36} Despite this interest and an abundance of research, considerable scatter is reported in values of $\Delta E_c$, ranging from a type-I junction with $\Delta E_c = 220$ meV to a type-II junction.\textsuperscript{37-42} These discrepancies are thought to be due to long-range CuPt-type ordering (LRO) which is known to reduce $\Delta E_c$.

The ability to lattice match to a mature technology like GaAs is particularly appealing for visible light emitters including light emitting diodes (LED)\textsuperscript{43} and heterojunction lasers.\textsuperscript{44} A concern relating to these devices is a sometimes-observed parasitic “deep emission” band at the GaAs-on-InGaP (ordered) interface. Explanations for this deep emission include an interfacial InGaAsP layer and a spatially indirect e-h transition across a type-II heterojunction.\textsuperscript{45,46,47} The explanation currently favored is a deep donor to deep acceptor transition in the GaAs well, which can be suppressed by the insertion of thin GaP layers.\textsuperscript{48}

The InGaP/GaAs system is an important material for solar cell applications.\textsuperscript{49} Tandem solar cells based on InGaP/GaAs, often with an AllnP windows acting as a diffusion barrier, exhibit efficiencies higher than 30%.\textsuperscript{50} In a tandem solar cell, demonstrated in Figure 1.2, multiple junctions are designed to absorb different parts of the electromagnetic spectrum. Higher band-gap InGaP formulates the top junction. Photons of lower energy are able to pass this junction and create electron-hole pairs (EHPs) in the lower band-gap GaAs junction below. The cost of these devices is considerable relative to conventional Si-based cells, which limits their usefulness to more
cost-insensitive applications such as providing energy needs for spacecraft and satellites.\textsuperscript{51}

The material properties of AlInP are less understood than those of InGaP. Despite this, as the \( y = 1 \) endpoint of the quaternary \((\text{Al}_y\text{Ga}_{1-y})_x\text{In}_{1-x}\text{P}\), the system is of interest for laser diodes and LEDs emitting in the orange-red range.\textsuperscript{52,53} The direct gap of \(\text{Al}_x\text{In}_{1-x}\text{P}\) is the largest of any non-nitride III-V; however, since \(\text{Al}_x\text{In}_{1-x}\text{P}\) is indirect for \(x > 0.44\), which includes the lattice-matched composition \(x = 0.52\), it is not of use as a direct optical emitter at this important mole fraction.\textsuperscript{54}
Above \( x = 0.44 \), \( \text{Al}_{x}\text{In}_{1-x}\text{P} \) \( \Gamma \)-valley cathodoluminescence emission is found to decay exponentially according to:\(^5^4\)

\[
I(x) = \frac{A}{1 + B \exp \left( \frac{E_{\Gamma}^0(x) - E_{\Gamma}^x(x)}{kT} \right)}
\]

(1.2)

Where \( B \sim (\tau_{\Gamma}/\tau_X)(m_{X}^*/m_{r}^*)^{3/2} \). Band behavior with mole fraction \( x \) is reported to fit well to a linear model, with \( \Gamma \) and \( X \) conduction-band minima having 300 K behavior given by:\(^5^4\)

\[
E_{\Gamma}^0(\text{Al}_x\text{In}_{1-x}\text{P}) = E_g^0(\text{InP}) + 2.23x \\
E_{\Gamma}^X(\text{Al}_x\text{In}_{1-x}\text{P}) = 0.18x + 2.24
\]

(1.3)

\( E_g(\text{InP}) \) is usually taken as 1.34 eV at 300 K. Al is highly reactive and susceptible to contamination, particularly of oxygen; therefore, it is the focus of considerable research to reduce the incorporation of these deep levels in the AlInP lattice.\(^5^5\),\(^5^6\)

1.2.2 Ordering in InGaP and AlInP systems

Many III-Vs, including InGaP and AlInP, exhibit long-range CuPt-type ordering. The CuPt-type ordered phase of \( \text{A}_x\text{B}_{1-x}\text{C} \) is marked by a monolayer superlattice along the [111] direction having alternating cation structure:

\[
A_{x+\frac{\eta}{2}}B_{1-x-\frac{\eta}{2}}^{x+\frac{\eta}{2}}B_{1-x+\frac{\eta}{2}}
\]

(1.4)
The order parameter $\eta$, where $0<\eta<1$, is a strong function of growth conditions including temperature, Group-V to Group-III beam pressure ratio, and substrate orientation.\textsuperscript{57} Generally, higher growth temperatures lead to a higher degree of ordering; therefore, at InGaP organometallic vapor phase epitaxy (OMVPE) growth temperatures of $\sim750^0\text{C}$, $\eta$ is typically 0.3-0.6,\textsuperscript{58} while at lower molecular beam epitaxy (MBE) growth temperatures $\eta \leq 0.3$,\textsuperscript{59} and often no ordering is observed.\textsuperscript{60} The ordering-associated doubling of the unit cell in the $[111]$ direction changes the periodicity and symmetry of the lattice. This doubling has a number of electronic effects, the most important being a valance-band splitting and a band-gap reduction.\textsuperscript{61-64} The band-gap reduction can be modeled by the equation:

$$E_g(\eta) = E_g(0) - \eta^2 [E_g(0) - E_g(1)]$$

(1.5)

For InGaP at 20 K, $E_g(0) = 2.005 \text{ eV}$ and $\Delta E = E_g(0) - E_g(1) = 0.471 \text{ eV}$.\textsuperscript{65} In higher mole fraction $\text{Al}_x\text{In}_{1-x}\text{P}$, significant long-range ordering is reported to produce a crossing of the reduced $\Gamma$-point and the X-band.\textsuperscript{61} This crossing results in direct optical transitions in an otherwise indirect material. Since ordering is a stable surface phenomena (i.e., during growth), but is not necessarily energetically favorable in bulk crystal structure, post-growth annealing tends to reduce the degree of ordering in both InGaP\textsuperscript{66} and AlInP.\textsuperscript{67} Conventionally, $\eta$ is determined using photoluminescence (PL) and Equation (1.5), though XSTM, Raman scattering, and diffraction techniques are also used among other methods.\textsuperscript{57,60,68}
1.2.3 Growth and Interdiffusion at InGaP/GaAs and AlInP/GaAs Junctions

Having an identical anion transition to the InGaAs/InP system discussed in Section 1.1, it might be expected that As-P exchange is a dominant interfacial reaction at InGaP/GaAs and AlInP/GaAs heterointerfaces. Indeed, a dependence of interface quality and charge density on As soak time in InGaP/GaAs heterostructures is reported, as is an As-P exchange mechanism.\textsuperscript{69,70} A similar asymmetrical interface behavior to the InGaAs/InP system is observed: P atoms are replaced by As during \( \text{As}_2 \) exposure, causing a transition layer to form at the GaAs-on-InGaP interface; however, some disagreement exists on whether or not \( \text{P}_2 \) exposure correspondingly degrades the InGaP-on-GaAs interface during growth by gas source molecular beam epitaxy (GSMBE).\textsuperscript{70-72} Mesrine \textit{et al.} observe monotonic red-shifts in the photoluminescence (PL) emission energy of InGaP/GaAs quantum wells when As exposure on InGaP is increased during chemical beam epitaxial (CBE) growth.\textsuperscript{73} Correspondingly, they observe PL blue-shifts with increasing P exposure on GaAs. These PL shifts are attributed to changes in the well dimensions as a function of interface soak time. To maintain abrupt interfaces, it is recommended that pre-growth soak times should be minimized and source interruption time for venting maximized.\textsuperscript{71} In addition to these exchange reactions, In is well known to segregate on the just-grown InGaP surface. This often leads to the incorporation of In into GaAs at the GaAs-on-InGaP interface.\textsuperscript{45,74} Using short 3s P and 5s As pre-exposures before InGaP and GaAs GSMBE growth respectively, Dong \textit{et al.} identify InGaAs-like interfaces at both InGaP-on-GaAs and GaAs-on-InGaP using cross-sectional scanning tunneling microscopy (XSTM).\textsuperscript{68} They note that the GaAs-on-InGaP interface has a wider transition region than the InGaP-on-GaAs interface, measuring approximately 3-4
atomic bilayers. Furthermore, they observe no evidence of As-P exchange at either interface. So, as in InGaAs/InP, the duration and dynamics of the growth transition may be a determining factor in which interfacial reactions occur and to what extent heterointerfaces are degraded. While less is reported on the AlInP/GaAs interface, similar cation and anion transitions make it reasonable to believe that similar interfacial reactions and behavior are possible.

1.3 Diffusion in III-V Semiconductor Alloys

1.3.1 Importance of Diffusion Research

The emergence of III-V semiconductors has brought about unprecedented advances in device engineering. The semiconductor heterojunction is a fundamental building block of these devices. As the trend of device miniaturization continues, interfacial behavior at high operating temperatures becomes increasingly important. Using a common applied power density of 5 W/mm, gap temperatures in GaN-based transfer length measurement (TLM) test structures are reported to be $400^\circ$C.\textsuperscript{75} Additionally, HEMT channel temperatures greater than $350^\circ$C during operation at 6 W/mm are estimated.\textsuperscript{76} In addition to high temperatures observed during device operating conditions, high temperatures used in the growth of III-V structures give rise to the potential for atomic cross-diffusion due to an interfacial atomic concentration gradient. During Ge growth on GaAs, changes in the growth temperature lead to cross-diffusion on a micron-scale.\textsuperscript{77} The effects of this diffusion are important to control in, for example, optical devices, where diffusion can alter well widths and emission spectra.\textsuperscript{78-82}
In electrical devices, diffusion can alter dopant profiles, lead to the homogenization and subsequent relaxation of strained materials, and introduce local dipoles that modify heterojunction band-offsets.\textsuperscript{83,84} Diffusion profiles are often measured electrically by four-point probe\textsuperscript{85} and C-V\textsuperscript{86} measurements (dopants), chemically by SIMS or Auger electron spectroscopy (AES), or optically via luminescence techniques such as CLS and photoluminescence spectroscopy (PLS) which excite transitions in quantum wells or superlattices.\textsuperscript{81,82}

1.3.2 Fickian Diffusion Theory

Fick’s law is the statement that atoms move according to a concentration gradient. This is expressed mathematically as:

\[ J = -D \nabla C \]  \hspace{1cm} \text{(1.6)}

In Equation (1.6), \( J \) is the flux of atoms at a point, \( D \) is a diffusion coefficient, and \( C \) is the concentration of atoms at the same point. From this a diffusion equation, Fick’s second law, can be derived (one-dimensional with concentration-independent \( D \)):

\[ \frac{\partial C}{\partial t} = D \frac{\partial^2 C}{\partial x^2} \]  \hspace{1cm} \text{(1.7)}

\[ D(T) = D_0 e^{-E_{\text{act}} / kT} \]  \hspace{1cm} \text{(1.8)}

In Equation (1.7), \( x \) is depth, \( t \) the diffusion time, \( E_{\text{act}} \) the activation energy for diffusion representing the minimum energy required to diffuse from one site to another, \( D_0 \) an experimentally determined constant, \( T \) temperature, and \( k \) the Boltzmann constant. While
Fick’s second law often oversimplifies or neglects important processes, it provides a useful starting point from which to model diffusion. While a one-dimensional treatment is often adequate in layered structures, it may be important to consider lateral variables when diffusion is performed with a mask. Boundary conditions determine the final solution of the diffusion equation. Perhaps the most important solution corresponds to a constant surface concentration $C_0$ with boundary conditions $C(x = 0, t) = C_0$ and $C(x > 0, t = 0) = 0$:

$$C(x,t) = C_0 \text{erfc} \left( \frac{x}{2\sqrt{Dt}} \right)$$  \hspace{1cm} (1.9)

This solution is often applicable in diffusions from the vapor phase, where $C_0$ will be determined by solid-vapor equilibrium relations and limited by the species’ solubility in the semiconductor. The assumption of a concentration-independent diffusion coefficient neglects many potentially important processes and must be qualified for a given experiment. By demonstrating a linear relationship between $4Dt$ and time, Gillin et al. verify a concentration-independent $D$ in In$_{0.66}$Ga$_{0.33}$As/In$_{0.66}$Ga$_{0.33}$As$_{0.7}$P$_{0.3}$ quantum wells annealed in the 800-900°C regime. While these concentration-independent processes do occur in certain regimes, diffusion processes frequently depend sensitively on the concentration of point-defects, dopants, and impurities, making the diffusion coefficient in Fick’s law a function of concentration. Experimentally, this concentration dependence often results in double diffusion profiles.
1.3.3 Diffusion in Semiconductor Lattices

Direct vacancy and interstitial movements are the most basic diffusion processes and form the building blocks of more complicated models. Vacancy diffusion describes the movement of atoms on unoccupied lattice sites. Interstitial diffusion describes the movement of atoms on sites between lattice atoms. Activation energies for vacancy mechanisms are typically an order-of-magnitude higher than those for interstitial mechanisms due to the relative ease of interstitial movement. A pure vacancy mechanism is proposed in certain temperature regimes at strained InGaAsP/InGaAs junctions, as well as in a number of self-diffusion studies; however, the creation of anti-site defects (e.g., a Group-III atom is substituted on a Group-V site) that result from nearest-neighbor vacancy movement in III-V compounds is energetically unfavorable. More often, vacancies and interstitial atoms, introduced into a material during growth or subsequent processing, are insufficient to describe diffusion in a semiconductor because of interactions between point-defects and concentration-dependences.

Frank-Turnbull and kick-out mechanisms operate in a number of III-V semiconductor materials. The Frank-Turnbull mechanism, written here for an atom (Group-II) which exists in a singly positive state interstitially, and a singly negative state when substitutional on a Group-III site, is characterized by the following reaction:

\[ s^- + 2h \leftrightarrow i^+ + v_{III} \]  

(1.10)

In Equation (1.10), \( s \) is a substitutional atom, \( h \) a hole, \( i \) an interstitial atom, and \( v_{III} \) a Group-III vacancy. Atoms diffusing by a Frank-Turnbull mechanism move interstitially before becoming substitutional on a vacancy site. This mechanism describes the
diffusion of some acceptor atoms and transition elements in zincblende III-Vs.\textsuperscript{90} Additionally, it may describe the low-temperature diffusion of P in GaAs\textsuperscript{91} and the incorporation of As into the InP lattice from a vapor phase.\textsuperscript{92} The kick-out mechanism, proposed to explain the diffusion of Zn in GaAs, is characterized by:\textsuperscript{93}

\[ i_D^+ \leftrightarrow s_D^- + i_L + 2h \]  \hspace{1cm} (1.11)

The reaction describes a diffusing interstitial atom displacing, or “kicking-out”, a lattice atom. The $D$ subscripts denote diffusing species while the $L$ subscript denotes a lattice atom and, as with the Frank-Turnbull reaction of Equation (1.10), the charge states can be modified according to the nature of the material and diffusion. The Frank-Turnbull and kick-out mechanism result in indistinguishable diffusion profiles because of the Frenkel process by which a lattice atom can form a vacancy-interstitial pair.\textsuperscript{90} The difference in the two processes is in their respective reaction products: every operation of the Frank-Turnbull reaction results in the loss of one vacancy, while every operation of the kick-out mechanism results in an additional interstitial atom. Ball et al. use a transmission electron microscope (TEM) to identify excess interstitial atoms on the diffusion front in Zn diffused GaAs, providing strong evidence for a kick-out mechanism in this system.\textsuperscript{94,95}

In materials where the majority carrier concentration is greater than the intrinsic concentration $n_i$ (extrinsic materials), the diffusion coefficient is almost always a function of doping. With reference to the Frank-Turnbull and kick-out reactions, a diffusion equation for the two mechanisms is derivable that is solvable by the Boltzmann-Matano technique.\textsuperscript{96} The diffusion coefficient $D(C)$ is found to be proportional to $p^\gamma$ (or $n^\gamma$ in n-
type materials), where $\gamma$ is the difference in electric charge between the substitutional and interstitial atoms. The Frank-Turnbull and kick-out processes are therefore fundamentally concentration-dependent in extrinsic semiconductors. Physically, this can be understood as an increase in the proportion of atoms in the mobile interstitial form with increasing doping. In intrinsic materials, where carrier concentrations are determined by $n_i$, the Frank-Turnbull and “kick-out” mechanisms are concentration-independent. In Zn-diffused GaAs the predicted $C^2$ concentration dependence (Zn$^-$ in the substitutional form and Zn$^+$ interstitially gives $\gamma=2$) in the extrinsic regime, coupled with a concentration-independent diffusion coefficient when $p$ falls below $n_i$, reproduces the observed double profile. Tuck et al. propose an alternate explanation by which diffusion in the bulk is limited by the material’s ability to produce the vacancies consumed by each operation of the Frank-Turnbull mechanism: In the near surface region there are an abundance of vacancies introduced by absorption from the vapor phase, and the expected $C^2$ profile results. In the bulk, however, the lower vacancy concentration results in a broader profile. This illustrates the confusion that can result from the similarity between Frank-Turnbull and kick-out diffusion mechanisms.

The dependence of the diffusion coefficient on carrier concentration above the extrinsic transition is known as the “Fermi-level effect.” While an important consideration, the extrinsic transition is only an issue at relatively high doping levels since intrinsic carrier concentrations at diffusion temperatures can be very high, $\sim 5 \times 10^{18}$ cm$^{-3}$ in InAs at 800°C for example. As the carrier concentration increases above the intrinsic level, the diffusion coefficient via charged point-defects is expected to scale as the power of the charge state of the defects. This is because the dissociation
reactions which create charged point-defects require a number of carriers $\gamma$ to maintain charge neutrality. The full diffusion coefficient (written for the GaAs system) according to this charged point-defect model is written below:

$$
D(E_f, P) = \sum_{\alpha, \beta, \alpha', \beta'} \left[ P_{As_4}^{1/4} \left( D^{\beta^-}_{V_{\alpha}, P_{\alpha} = 1} \left( n_1 \right) \left[ \frac{n}{n_i} \right]^{\gamma} \right) + D^{a^+}_{\alpha, P_{\alpha} = 1} \left( n_1 \right) \left[ \frac{P}{n_i} \right]^a \right] 
+ P_{As_4}^{-1/4} \left[ D^{\alpha^+}_{\beta, P_{\beta} = 1} \left( n_1 \right) \left[ \frac{P}{n_i} \right]^a + D^{b^+}_{\beta, P_{\beta} = 1} \left( n_1 \right) \left[ \frac{P}{n_i} \right]^b \right].
$$

(1.12)

The equation effectively states that, in the extrinsic regime, diffusion on both sublattices is controlled by charged point-defects with the power law of the dependence determined by the charge states present. The charges on various point-defects are identified by $\alpha, \beta = \text{Group-III interstitial and vacancy, respectively, and } a, b = \text{Group-V interstitial and vacancy, respectively.}$ The $P_{As_4}^{\pm 1/4}$ pressure dependences arise from the enhancement or suppression of vacancies that comes from changing the ambient, in this case As$_4$, pressure. Increasing $P_{As_4}$ increases the number of Ga vacancies and As interstitials; correspondingly, this decreases the number of Ga interstitials and As vacancies. As exists as As$_4$ in the vapor phase, hence the fourth-root dependence. It is important to note that the model predicts a concentration-dependence for vacancy/interstitial involved diffusion which occurs on the Group-III and V sublattices with extrinsic doping (i.e., it is not limited to dopants). It can be seen that for $n$ or $P < n_i$ there is, as expected, no significant modification of $D$ through charged point-defects. This model explains the As$_4$ pressure-dependence of $n$ and $p$-type enhancement of diffusion in GaAs/AlGaAs superlattices. A double profile can be explained by the Fermi-level effect. In doped
materials a constant diffusion coefficient is expected for carrier concentrations less than the intrinsic doping. In the extrinsic regime, where carrier concentrations are above $n_i$, the semiconductor may exhibit a concentration-dependence owing to added impurity terms in $D$. Deeper in the material, where dopant levels are below $n_i$, the concentration-dependence of $D$ drops out. This result is the basis of research in the impurity-induced layer disordering (IILD) of quantum-well structures, where researchers change energy gaps and refractive indices in selectively diffused regions.

Diffusing species often form complexes which facilitate their movement through the lattice. Pure substitutional-vacancy interactions are referred to as “uncorrelated” because the net movement of a substitutional atom requires the dissociation of the $s-v$ pair and the substitutional atom jumping to a different vacancy site. Without any interaction with a new vacancy the pair continues to change place, resulting in no net movement. A ring mechanism refers to a vacancy-assisted diffusion by which a substitutional impurity couples strongly enough with the vacancy to travel through the crystal as a pair. This mechanism requires the partial dissociation of the pair while the vacancy travels to, at least, the third nearest-neighbor atom to produce one net movement of the substitutional atom. The ring mechanism is diagramed in Figure 1.3. One movement of a substitutional atom via a ring mechanism in a III-V compound creates a large number of anti-site defects and is energetically unfavorable. Another series of movements eliminates anti-site defects by restoring ring atoms to a site on their original lattice. A ring mechanism is an important mechanism for impurity diffusion in Si and is proposed for P in GaAs.
Figure 1.3: Movement of a substitutional (red) atom-vacancy pair through the lattice via a ring mechanism on the (111) plane. An additional movement will restore the created anti-site defects.\textsuperscript{101}

The formation of a divacancy, shown in Figure 1.4, may facilitate diffusion in some materials owing to the smaller degree of lattice distortion required for movement.\textsuperscript{102}

Figure 1.4: Movement of a substitutional atom via a divacancy mechanism on the (111) plane.\textsuperscript{90}

Mechanisms involving both nearest-neighbor and second-nearest neighbor divacancy complexes are observed more often than pure vacancy or ring mechanisms in III-Vs as they don’t involve the formation of significant numbers of anti-site defects. Divacancy mechanisms are proposed to explain the diffusion of many donors in III-V materials,\textsuperscript{90} additionally, there are published reports that the diffusion of lattice atoms such as In in InSb,\textsuperscript{103} as well as the Si-enhanced mixing at low temperature InGaAs/InP interfaces,\textsuperscript{104} involve divacancies. Van Vechten proposes a theory by which doping can produce the
expected enhancement of ring and divacancy-mediated diffusion by lowering the energy of formation of anti-site defects.\textsuperscript{105}

That members of the same period tend to diffuse by the same mechanism raises the question of what predictors of diffusion mechanisms exist. Certainly atomic site is important, but atomic radius is as well. It is counter-intuitive that donor atoms, which tend to be smaller, diffuse not interstitially but often by the formation of a divacancy complex, while acceptor atoms, larger in general, diffuse through a substitutional-interstitial mechanism. The primary reason for this is in the charge states of these atoms in the lattice. Group-II acceptor and Group-VI donor atoms tend to take on respective positive and negative charges in the III-V lattice. The Group-IV atoms tend to substitute on a site of comparable size (i.e., larger atoms prefer to substitute on the larger Group-III sites) forming a positively-charged ion. These positive ions are typically smaller than the negatively-charged ions and are more able to diffuse interstitially. Interstitial movement of the negative ions requires larger lattice distortions than their diffusion via a divacancy mechanism.

1.3.4 Controlled Diffusions

A number of studies on diffusion in III-Vs exist which report widely varying quantitative results. As the difficulties in performing a controlled and repeatable anneal account for some of this variation, it is worthwhile to discuss the annealing processes by which diffusion is induced. Controlled diffusions are sometimes carried out in an ampoule of known volume inside a furnace. A diffusion source, intended to produce mobile elemental species which can enter the semiconductor surface from the vapor
Perhaps most important for a simple diffusion experiment is controlling the number of thermodynamic free parameters $F$ according to Gibb’s phase rule:

$$F = C - P + 2$$  \hspace{1cm} (1.13)

In Gibb’s phase rule, $C$ is the number of elemental components in the system and $P$ the number of phases present. In order for diffusion to proceed in a well-defined and repeatable manner, the number of thermodynamic free parameters should be reduced to zero.\textsuperscript{106} Setting the temperature and pressure of one constituent in a binary III-V compound diffusion is adequate to satisfy $F = 0$.\textsuperscript{106}

Schottky (surface) and Frenkel (bulk) mechanisms determine point-defect concentrations, written here for the binary compound $AB$:

$$
\begin{align*}
A_v + V_A & \leftrightarrow A_S \\
B_v + V_B & \leftrightarrow B_S \\
A_s & \leftrightarrow I_A + V_A \\
B_s & \leftrightarrow I_B + V_B
\end{align*}
$$

(1.14)

The first two (Schottky) reactions describe an atom at the surface of the solid phase (subscript $S$) being desorbed from the solid to form a vacancy on its sublattice, along with a vaporous atom (subscript $V$). These created vacancies are free to diffuse into the crystal. The third and fourth (Frenkel) reactions describe the bulk creation of an interstitial-vacancy pair by a lattice atom. It is desirable to approach solid-vapor equilibrium quickly, typically by adding enough of the Group-V element (which usually has a non-negligible partial pressure) to prevent significant desorption from the semiconductor. Desorption can lead to a loss of stoichiometry and stability in the
semiconductor; correspondingly, metal will pool on the surface as Group-V elements leave. With reference to a phase diagram, and access to data for partial pressures and solubilities, the desired amounts of added materials may be calculated.

Not surprisingly, the bulk of the research on III-V diffusion is driven by related problems in device research. For many systems there is controversy surrounding not only quantitative results by what fundamental mechanisms operate. Activation energies for Fickian interdiffusion in InGaAs/InP quantum-wells are reported that vary from 1.7-5.8 eV. Some authors suggest a low-temperature Frank-Turnbull mechanism, and recently it is proposed that Fickian diffusion doesn’t operate in this system at $T<T_c$. Much of the discrepancy results from different annealing conditions. Satisfying $F = 0$ in Gibb’s phase rule which, in turn, establishes point-defect concentrations in a well-defined and reproducible way, can be difficult with complex heterostructures as the number of elemental species directly increases the number of free thermodynamic parameters that need to be controlled; therefore, experimenters tend to look for ways to sidestep this requirement like annealing under an inert cap or annealing with structures oriented face-to-face, so that vaporous Group-V atoms produced might replace each other at the surfaces of interest.

1.3.5 Annealing Under an Inert Capping Layer

While phase diagrams, partial pressures, and solubility tables, can be found for common dopant diffusions, they might not exist for diffusions designed to explore the cross-incorporation of principal lattice atoms. In these situations experimenters often choose to sidestep solid-vapor equilibrium by the growth of an inert cap or surface
passivation layer. While this does preclude some Schottky reactions, particularly Group-V out-diffusion, it should be noted that diffusion will proceed with a different dynamic than in non-capped structures. It is reported that the diffusion coefficient for Al-Ga cross-diffusion at Al$_x$Ga$_{1-x}$As/GaAs junctions is a strong function of the encapsulation condition, as well as the encapsulation material itself. Guido et al. note an order of magnitude higher diffusion coefficient when annealing these junctions under a Si$_3$N$_4$ cap relative to SiO$_2$. This is explained by either an IILD effect from Si diffusing directly from the capping layer throughout the structure, or as a consequence of Ga passing through the SiO$_2$ layer and leaving Group-III vacancies through which diffusion can occur.
CHAPTER 2

EXPERIMENTAL TECHNIQUES

2.1 The Ultra-High Vacuum Condition

In semiconductor analysis it is often critical to maintain a surface free from contaminants. Surface adsorbates in concentrations as low as 0.2-0.5 monolayers can pin the semiconductor Fermi-level and introduce surface dipoles that affect later measurements.\textsuperscript{110-113} These adsorbates, generally of unknown composition and structure, can modify Schottky barrier heights and surface structure.\textsuperscript{114} While sputtering away adsorbate layers is possible, this often leads to an undesirable intermixing of the semiconductor lattice; therefore, it is preferable to maintain clean surfaces by avoiding adsorbate buildup. At typical high vacuum conditions of $10^{-6}$ torr, a monolayer of adsorbate (with unity sticking coefficient) forms approximately every second.\textsuperscript{115} To maintain a clean, adsorbate-free surface for the hour-scale time periods of many experiments, ambient pressures on the order of $10^{-10}$ torr, or ultra high vacuum (UHV), are required.

These pressures are maintained by the use of stainless steel analysis chambers and a series of pumps. Basic roughing (rotary) pumps operate from atmospheric pressure to approximately $10^{-3}$ torr. They also serve the purpose of backing turbomolecular pumps, which use a high speed rotor to evacuate gas molecules and achieve pressures as low as
$10^{-9}$ torr. Below these pressures ion pumps are used to achieve UHV conditions. Ion pumps rely on high speed electrons moving in a magnetic field to ionize residual gas molecules. Ionized gas molecules are then subject to and trapped by an applied potential. In the Electronic Materials and Nanostructures Laboratory (EMNLab) at The Ohio State University (OSU), cryopumps and Ti-sublimation pumps are also occasionally used for the removal of gas molecules. Pressures on the scale of $10^{-10}$ torr are the norm, thereby ensuring a clean analysis surface.

2.2 Secondary Electron Microscopy

The scanning electron microscope (SEM) is an invaluable tool in a number of fields where nanoscale characterization is critical. Electrons are emitted either thermionically or by a field emission mechanism in a high vacuum environment. These electrons travel through a series of electrostatic lenses and scanning coils which raster a primary beam across the sample surface. Secondary electrons are detected by a scintillator-photomultiplier system and produce an image of the scanned surface. Because the electron beam can be tuned to a nanometer-scale diameter, high resolution images are possible. Incident electrons interact with solids by a number of mechanisms other than secondary electron emission. These include but are not limited to the production of characteristic x-rays, Auger electrons, and, through the creation of EHPs, photons that correspond to band-gap or sub band-gap energies; therefore, the SEM can be used as a platform from which to study a number of interactions with high resolution.
In EMNLab a JEOL JAMP-7800F UHV Auger microprobe is used. This is a field emission microprobe that is shown in Figure 2.1. The microscope includes an optical chain and hemispherical analyzer for CLS and AES respectively, which are discussed in more detail in sections 2.3 and 2.4.

Figure 2.1: JEOL JAMP-7800F field emission UHV SEM used in EMNLab. Important components of the SEM are labeled.

The incident electron probe can be varied in energy from 0.1-25 keV, currents varied from $10^{-11}$ to $10^{-7}$ A, and magnification from X20 to X300000. The incident probe diameter defines the resolution of the instrument and is a strong function of these
variables. Beam diameter as a function of the primary beam parameters is shown in Table 2.1, which demonstrates that the beam can be tuned to < 5 nm.

<table>
<thead>
<tr>
<th>Beam Voltage</th>
<th>10 pA</th>
<th>1 nA</th>
<th>10 nA</th>
<th>50 nA</th>
<th>100 nA</th>
<th>1µA</th>
</tr>
</thead>
<tbody>
<tr>
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<td>4 nm</td>
<td>6 nm</td>
<td>10 nm</td>
<td>30 nm</td>
<td>80 nm</td>
<td></td>
</tr>
<tr>
<td>10 kV</td>
<td>8 nm</td>
<td>10 nm</td>
<td>20 nm</td>
<td>60 nm</td>
<td></td>
<td></td>
</tr>
<tr>
<td>5 kV</td>
<td>14 nm</td>
<td>15 nm</td>
<td>43 nm</td>
<td>140 nm</td>
<td></td>
<td></td>
</tr>
<tr>
<td>3 kV</td>
<td>18 nm</td>
<td>20 nm</td>
<td>52 nm</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Table 2.1: SEM primary electron beam diameter versus excitation condition.

The JEOL JAMP-7800F can also be used for electron beam induced current (EBIC) measurements of defect distributions and minority carrier dynamics. Samples can be mounted in either plan-view or cross-section and cooled to 10 K with liquid helium (LHe). An attached processing chamber allows for in-situ cleaving, metal deposition, and annealing treatments, without breaking UHV conditions. Additionally, an Ar⁺ sputter gun is used for AES sputter depth profiling, the removal of surface contamination, and charge compensation in insulator analysis.

2.3 Cathodoluminescence Spectroscopy

Cathodoluminescence spectroscopy is similar to photoluminescence spectroscopy (PL), but involves primary electron rather than photon excitation. An electron entering a semiconductor may lose its energy via a number of processes which form the basis for a
wide variety of analysis techniques. One of these processes is the generation of EHPs which eventually recombine and produce optical emissions. These emissions are measured by an appropriate detector and form the basis of CLS. Plasmon-scattering is the dominant energy loss mechanism in the $10^2$-$10^4$ eV regime typically used and is responsible for the creation of the majority of EHPs.\textsuperscript{116} The threshold energy for EHP creation is above the semiconductor band-gap ($E_g$) due to the inelastic nature of most collisions. This energy is material dependent and is given by $E_i = 2.8E_g + M$, where $0 < M < 1$ eV.\textsuperscript{117}

An electron’s mean-free-path in a solid is proportional to its energy. This makes CLS unique in its ability to gather depth-resolved information in a non-destructive manner. Everhart and Hoff studied the relationship between electron mean-free-path and energy in 1971.\textsuperscript{118} The Everhart-Hoff model starts with an expression of energy loss per unit length:

$$-rac{dE}{ds} = (2\pi N_A e^4) \left( \frac{Z\rho}{A} \right) \left( \frac{1}{E} \ln \left( \frac{aE}{I} \right) \right)$$ \hspace{1cm} (2.1)

In Equation (2.1), $N_A$ is Avogadro’s number, $I$ is the $Z$-dependent mean excitation loss energy, $\rho$ is the material density, $A$ is atomic weight, $Z$ is atomic number, and $a = 1.1658$. From this model is derived the maximum range for incident electron penetration:
\[ R_B = \int_0^\infty \frac{\partial E}{\partial (\rho^2)} = \int_0^{\xi(E_0)} \xi \partial \xi = \int_0^{\ln(\xi)} \ln(\xi) \]  \hspace{1cm} (2.2)

In Equation (2.2), \( \xi = aE/I \) and \( E_B \) is the incident beam energy. For the energies 5-25 keV and atomic numbers 10<Z<15 a useful approximation for this range is:\(^{118}\)

\[ R_B^{E-H} = \frac{0.0398}{\rho} E_b^{1.75} (\mu m) \]  \hspace{1cm} (2.3)

Separately, a range approximation is proposed by Kanaya and Okayama (1972) which provides accurate results for a wider range of atomic numbers\(^{119}\):

\[ R_e^{K-O} = \frac{0.276 A}{\rho Z^{0.889}} E_b^{1.67} (\mu m) \]  \hspace{1cm} (2.4)

Everhart and Hoff empirically propose a universal depth-dose function \( g(z) \) versus electron energy:\(^{118}\)

\[ g(z) = 0.60 + 6.21z - 12.40z^2 + 5.69z^3 \]  \hspace{1cm} (2.5)

In the depth-dose function \( z \) is normalized to \( R_B \) and 0<z<1.

In practice, a Monte Carlo simulation such as that provided by the CASINO\(^{120}\) program is often easier to use and more accurate than the above models. CASINO simulates 0.1 - 30 keV electron trajectories in a layer structure entered by the user. In addition to electron energy loss information, CASINO provides backscattered electron distributions, backscattering coefficients, and x-ray emissions, as well as important information about recombination volume and lateral electron-beam spreading, which vary dramatically with atomic number. In general, excellent agreement is found between
observed semiconductor emissions and CASINO predictions. A CASINO simulation for electron beam penetration versus energy in GaAs is shown in Figure 2.2, along with a comparison of the result derived from the depth-dose curves of Equation (2.5). Good agreement is found between the two methods, the Everhart-Hoff depth-dose curves tending to be slightly shallower than the CASINO models.

Figure 2.2: Maximum electron range (left) calculated from the Everhart-Hoff approximation in Equation (2.3). On the right, depth dose curves (dashed lines) calculated from Equation (2.5) are shown versus CASINO Monte Carlo simulations (solid lines) in GaAs.

Photoluminescence spectroscopy (PL) relies on the generation of EHPs by injected photons, typically at a single wavelength by a laser source. It is advantageous to choose a laser energy slightly greater than the band-gap energy of the sample. This
makes the choice of laser material-dependent and difficult for the study of wide-gap semiconductors. Since electrons used for CLS typically have energies $\geq 100$ eV, all pathways in semiconducting materials are accessible. Beyond its depth profiling capability, CLS has a number of other advantages versus photoluminescence and similar spectroscopies: since incident electrons are often several keV, generation rates and, correspondingly, signal-to-noise ratios, can be high. The generation rate for electron-hole pairs is given by:\textsuperscript{121}

$$G = \frac{V_b I_b (1 - \gamma)}{eE_i}$$

(2.6)

In Equation (2.6), $V_b$ is the electron-beam voltage, $I_b$ is beam current, and $\gamma$ is the fractional electron beam energy loss due to backscattering. EHP Generation rates for CLS are typically $> 10^{12}$ sec$^{-1}$.

CLS emission can be intrinsic or extrinsic. Intrinsic luminescence refers to emission that is an intrinsic property of the material (e.g., band edge luminescence). While both direct and indirect-gap semiconductors exhibit intrinsic luminescence, it is of considerably lower intensity in the latter due to requirement for phonon participation. Cathodoluminescence is strongly dependent on temperature. Low temperatures offer several advantages including an increased signal-to-noise ratio and the minimization of thermal broadening. The increase in signal-to-noise ratio is due to an increase in radiative efficiency from a lower phonon occupation number.\textsuperscript{122} Additionally, peak sharpness is enhanced by the decreased conduction band filling resulting from electron beam excitation. Low temperatures can reveal other intrinsic electronic interactions such
as excitonic states. Excitons are electron-hole bound states which form when $k_B T$ is less than the ionization energy of the pair. Excitonic emission is typically close to the gap energy.\textsuperscript{123}

Extrinsic luminescence refers to recombination and emission via intentionally and unintentionally introduced lattice defects and impurities. Often these complexes quench luminescence by introducing non-radiative pathways, though they potentially introduce new radiative recombination processes. Because of the wide array of potential dopants and defects, a considerable number of these features often exist.

In EMNLab a JEOL JAMP-7800F UHV scanning electron microscope (SEM) is used as an electron source. The focusing optics of the SEM allow for the nanoscale characterization necessary for modern semiconductor devices. Optical emissions are collected via an Oxford MonoCL system consisting of a parabolic mirror set in UHV which focuses collected light though a quartz window at the vacuum-air interface. An Oxford grating monochromator allows photons of a selected wavelength to pass into the appropriate detector. For photon energies less than ~1.40 eV, a high-purity germanium (HPGE) detector is used. Above these energies a cooled photomultiplier tube (PMT) provides photon detection. This system is diagrammed in Figure 2.1. An additional benefit of using an SEM as the electron beam source is the ability to spatially resolve particular emissions using CL imaging or line scans. In these applications the beam is rastered or directed across the sample surface while a monochromator passes photons of a specific energy (panchromatic detection is also possible). By this means the spatial distribution of the monitored emission is obtained.
While the incident electron beam can be focused to a very small (~5 nm) diameter, shown in Table 2.1, it is important to realize the resolution-limiting factors of CLS. The size of the EHP generation volume limits the resolution of the technique but can be modeled with CASINO simulations. A CASINO simulation for a 5 keV, 1 nA beam in GaAs is shown in Figure 2.3 and demonstrates how lateral beam spreading information is obtained. CASINO models allow the experimenter to choose the optimum balance between signal and resolution for the particular application. In addition to beam spreading effects, generated carriers migrate via diffusion; therefore, it is important to determine how the resolution-limiting minority carrier diffusion length affects measurements.

Figure 2.3: CASINO simulation showing the percentage of electron energy given up within an indicated distance from an incident 5 keV, 1 nA electron beam in GaAs. Contours representing 50, 75, 90, and 95% are labeled.
2.4 Auger Electron Spectroscopy

Auger electron spectroscopy (AES) is an electron beam based spectroscopy which utilizes the Auger excitation process. Auger emission is a three-stage process where: (1) an incident electron knocks out a core level electron, (2) a higher level electron drops down to fill the level left by the first electron, and (3) gives up its energy to a third electron which is emitted and detected. Fundamentally, the transition by which an Auger electron is emitted is facilitated by the Coulomb interaction. The particular Auger process is named according to the core levels involved; thus, a transition where a K-level electron is knocked out, an L-level electron takes its place, and an L-level electron is emitted, is denoted a KLL transition. The emitted Auger electrons have a precisely defined kinetic energy corresponding to known atomic core-levels; however, subsequent scattering randomizes these energies. Because of this, only electrons emitted from the top few atomic layers of the sample escape without scattering; therefore, AES is an extremely surface-sensitive technique. Since atomic core levels are unique to a particular element, AES provides a powerful tool for surface chemical composition and uniformity analysis. The detection threshold for AES is approximately 1%, making it useful for the characterization of primary lattice elements, but not sensitive enough to resolve dopant or impurity atoms.

Energy conservation can also be satisfied via characteristic X-ray photon emission, though X-rays typically come from much deeper depths of 0.1-10 µm. Auger transitions are close in energy to X-ray transitions, but differ slightly due to the doubly ionized nature of the atom. For a KL₁L₂ process in an atom with atomic number Z, the Auger electron energy is: \[ E_{\text{Auger}} = ... \]
\[ E_{K,L_1,L_2}^Z = E_K^Z - E_{L_1}^Z - E_{L_2}^Z - \Delta E(L_1L_2) \]  \hspace{1cm} (2.7)

The first three terms are simply the characteristic X-ray energies, while the correction term \( \Delta E(L_1L_2) \) reflects the increase in binding energy of the \( L_2 \) electron when the \( L_1 \) electron is removed.\textsuperscript{115}

For quantitative AES, relative sensitivity factors (RSF) can be used to provide approximate elemental abundances. The concentration of element \( X \) in a given sample is:\textsuperscript{124}

\[ C_X = \frac{I_X}{\sum_a S_a d_a} \]  \hspace{1cm} (2.8)

In Equation (2.8), \( C_X \) is the atomic concentration of the species of interest, \( S_X \) is the relative sensitivity factor available from published tables, \( I_X \) is the experimentally measured relative Auger peak-to-peak amplitude, and \( d_X \) is a relative scale factor that includes data collection and beam parameters such as primary energy and current. Since the parameters of \( d_X \) are typically constant during analysis this factor usually cancels out of Equation (2.8). The summation is over one peak per element. This method suffers from matrix effects due to variations in electron escape depth and backscattering, chemical effects which can alter peak shapes and lead to errors in \( I_X \), and effects from surface topography. Despite these issues, Equation (2.8) often provides a useful starting point for quantitative analysis without standards.\textsuperscript{124}
Using the JEOL JAMP-7800F, AES can be performed in parallel with other electron-beam spectroscopies such as CLS. Electron energies are measured by an attached hemispherical analyzer, where data is collected as the bias on the analyzer walls is swept through a range which passes electrons with a narrow band of energies per unit time. The analyzer utilizes multiple detection by plural electron multipliers and is tunable from 0 to 3 keV with energy resolution 0.05 to 0.5%. Because of the high background secondary electron count AES data is sometimes presented in derivative mode (dN(E)/dE). For the spatial localization of elements, the primary electron beam may be rastered or positioned to produce an Auger image or line scan.

AES can be combined with Ar\(^+\) sputtering to provide depth profiles or to remove surface contamination. Typical sputtering energies are from 500 to 4000 eV. One of the most important applications of AES is to verify the cleanliness of semiconductor surfaces after cleaving or sputtering in ultra high vacuum (UHV). Figure 2.4 shows peaks corresponding to primary elemental constituents and contaminants in AlInP/GaAs DHs before and after sputtering, thereby demonstrating the ability of AES to measure the presence of contaminants and to monitor contaminant removal or, in the case of in-situ cleaving, ensure that contamination has been avoided.
Figure 2.4: AES spot-mode spectra taken on GaAs and AlInP \{110\} surfaces cleaved \textit{ex-situ} and sputtered to remove contamination. Primary elemental constituents can be identified and C and O-related adsorbates removed. AES is able to verify this removal as demonstrated by the decrease in O and C intensity after sputtering (red curve).

2.5 Secondary Electron Threshold Measurements

Secondary electron threshold (SET) measurements are a technique by which the work function of a semiconductor is measured by monitoring the onset of the secondary electron distribution under electron beam bombardment. The technique was originally applied to the measurement of metal work functions, and is being extended to semiconductor systems at EMNLab.\textsuperscript{125} The linear edge of the secondary electron threshold is extrapolated to the baseline of an energy versus intensity plot. This gives the secondary electron onset of Equation (2.9), shown below:
\[ \Delta E = \Phi_S - \Phi_A + V \]  

(2.9)

\( \Delta E \) is defined as the difference between the metal and analyzer work functions (subscripts S and A respectively) plus any applied bias \( V \) to raise the energy levels of the sample relative to the analyzer. The applied bias ensures that the lowest energy secondary electrons reach the detector.

The technique is relevant to semiconductor systems as depicted in Figure 2.5. While the electron analyzer work function is assumed constant over the time scale of the measurement, the semiconductor work function depends on the position of the conduction band edge \( E_c \) relative to the Fermi-level \( E_F \), as well as the electron affinity \( \chi \). In other words, SETs measure the semiconductor \( E_{\text{vac}} \) relative to \( E_F \) with a constant, measurable offset. If this offset is known \( E_{\text{vac}} \) may be determined and, with known \( E_c - E_F \), the electron affinity can be measured. Alternatively, with known \( \chi \) the position of \( E_c \) relative to \( E_F \) can be measured.
Figure 2.5: Pictorial description of the SET measurement in semiconductors. The quantity $\Delta E$ is measured which provides information about $E_{\text{vac}}$ and $E_c$. Superscripts S and A denote semiconductor and analyzer quantities, respectively.

Changes in the surface Fermi-level position due to contamination or Fermi-level pinning will change the local SET measurement. To minimize these effects, heterostructures are cleaved *in-situ* to yield a clean, contaminant-free surface. Surface cleanliness can be verified upon specimen introduction or at any subsequent time by AES. The unpinned nature of the surface is of critical importance to SET measurements as it is assumed that the measured surface characteristics are unchanged from the bulk value. The \{110\} surfaces of many III-V semiconductors undergo a reconstruction such that no surface states exist in the band-gap; therefore, no pinning of $E_F$ is observed at
these surfaces. In GaAs, As atoms are raised relative to surface Ga atoms to make an angle of approximately $27^\circ$ as shown in Figure 2.6.

![GaAs (110) surface reconstruction](image)

Figure 2.6: GaAs (110) surface reconstruction. The \{110\} surfaces of many III-V compounds, including GaAs and InP, are non-polar cleavage planes. This surface configuration leaves no electronic states in the band-gap.

A surface without cleavage-related ridges is necessary for accurate measurements since a high step density resulting from a poor cleave is known to introduce acceptor-like states with energies close to mid-gap. To promote a defect-free cleave along the desired plane, the substrate (i.e., the non-growth surface) is scored with a diamond scribe before moving the sample into the SEM processing and analysis chambers. Cleaves are performed with a pendulum-style apparatus incident on the top of the sample above the score mark. Cleave quality is initially assessed in the SEM. Because the SEM-observed secondary electron intensity is sensitive to changes in work function on the sub-10 nm scale, cleavage artifacts which can significantly affect the surface potential distribution are imaged and avoided. The effect of cleavage-related artifacts is shown in Figure 2.7, where cleave ridges modify the local $E_F$ and SET measurement. Since these ridges are monitored using the nm-scale resolution of the SEM, they can be avoided.
Figure 2.7: SEM image (left) and SET spot-mode scans (right) of an in-situ cleaved AlInP/GaAs DH. The SEM image shows cleave-related ridges in the substrate and on either side of the GaAs layer, along with the SET analysis points. The SET changes with respect to these SEM-observed features in a repeatable way.

The size and energy distribution of the incident electron beam determines the resolution of the SET technique. A beam of 3-5 kV provides the best combination of signal and resolution. CASINO simulations, shown in Figure 2.8 for InP, demonstrate that ~95% of all backscattered electrons come from within 60 and 130 nm of an incident 15 nm 3 and 5 kV beam, respectively. This number is used to estimate the diameter over which secondary electrons emerge.
Gao\textsuperscript{131} \textit{et al.} have done considerable work on the behavior of SET measurements across semiconductor junctions with various surface and beam conditions. Figure 2.9 shows the results of a series of SET measurements taken across a GaAs p-n junction, compared to theoretically calculated work functions assuming $\chi = 4.07$ eV and $E_g = 1.43$ eV. Gao finds reasonable agreement between SET measurements and theoretical results. Discrepancies are attributed to Fermi-level pinning caused by cleavage-related defects and contamination. In the same reference, Gao examines the possibility of using \textit{ex-situ}, air-cleaved, samples or sputtering to eliminate the difficult \textit{in-situ} cleaving step. It is found that Ar$^+$ sputtering pins the Fermi-level near mid-gap.
Figure 2.9: SET-measured versus theoretical work function for a cross-sectional (110) GaAs p-n junction cleaved in-situ. The SET measurements, from Gao et al., show reasonable agreement with the theoretical value.\textsuperscript{131}

It is important to consider the effects of primary electron beam conditions on SET measurements. Injected electrons disturb the equilibrium Fermi-level position if the generated EHP density is on the order of the doping. This can be estimated using Equation (2.6). For a 5 kV, 1 nA beam, carrier generation is \textasciitilde2\times10^{11} \text{cm}^{-3}, however, this estimate is probably low due to the large error in the estimate of the volume over which carriers recombine. In practice, the primary beam energy can simply be cycled and changes in the onset monitored. No change under a low excitation condition suggests a low-level-injection regime. Additionally, the incident electron beam can cause the buildup of surface carbon contamination by residual gas decomposition.\textsuperscript{131}
The use of SETs in measuring heterojunction properties is being examined at EMNLab and, at this point, has been used to measure variations in work function across CuInGaSe$_2$ grain boundaries, and the band-bending induced by metal deposition on GaN.\textsuperscript{132,133} By monitoring the change in SET as the electron beam is positioned at points across an interface, the band-offset $\Delta E_c$ may be able to be determined. For these measurements, doping should be kept low to keep depletion regions as large as possible; however, this low doping increases the probability that sample charging or high carrier injection levels will alter the energy of ejected secondary electrons.\textsuperscript{124}

2.6 Secondary Ion Mass Spectrometry

Secondary ion mass spectrometry (SIMS) is a widely used technique for the high resolution analysis of elemental composition. In SIMS, secondary ions are ablated from the sample surface under primary ion bombardment before being detected and resolved by a mass spectrometer. While detection levels vary considerably based on the element or compound of interest and the underlying matrix, the technique is capable of detecting elements in concentrations as low as $10^{16}$ cm$^{-3}$, making SIMS among the most sensitive tools for compositional analysis.\textsuperscript{115}

SIMS is performed in two basic modes, static and dynamic. Static SIMS analysis is fast relative to material decomposition and damage is confined to the top monolayer of a sample. The static SIMS limit is defined by the highest excitation conditions under which each ejected secondary ion comes from an undamaged portion of the material (i.e., less than a monolayer of material is removed). Since beam currents in many instruments can be varied over several orders of magnitude, surface particle lifetimes can be made
slow enough for minimum damage (static SIMS), or fast enough for sputtering (dynamic SIMS). Above the static limit SIMS is operating in dynamic mode where the surface is deliberately sputtered to provide depth-resolved material characterization.

SIMS operates by the detection of ionized secondary species. Ionized species typically account for less than 1% of ejected material from clean metal surfaces. The primary ion (analysis) beam is sometimes interlaced with dedicated sputter ion beams which, in addition to quickly ablating surface material, enhance the secondary ion yield of certain lattice species by several orders of magnitude as they themselves become implanted. Oxygen ($O^+$) sputtering is known to increase the secondary ion yield of certain positively charged species due to its high electronegativity, while $Cs^+$ sputtering increases the secondary ion yield of some negatively charged species due to its electropositivity. The relationship between sputtering element and increased secondary ion yield is demonstrated in Figure 2.10.
SIMS is strongly dependent on matrix effects. Matrix effects refer to the dependence of the relative sensitivity factor for a particular element on the concentrations of other elements in a sample. Matrix effects make quantitative SIMS analysis difficult without the use of standards having known concentrations of elements in an applicable matrix. In lieu of standards, an approach sometimes used is to monitor CsM$^+$ (positively charged cesium-metal) ions which result from bonding with a Cs$^+$ sputter source. It is reported that these ions are not sensitive to matrix effects (i.e., the ratios of atomic species are linear with concentration). This method suffers from the drawback that ion yields for CsM$^+$ are typically low.
Sputtering itself can introduce significant smearing at semiconductor interfaces, which increases with the number of previously sputtered layers (i.e., the sputtering depth). In samples exhibiting flat surface topography, depth resolution is improved by reducing the energy of the primary ion beam; however, this correspondingly reduces the sputter rate, so it is experimentally important to find the optimum balance between a reasonable sputter rate and depth resolution.

A PHI TRIFT III time-of-flight SIMS (TOF SIMS) is used in EMNLab. This system is diagrammed in Figure 2.11.

Figure 2.11: PHI TRIFT-III TOF SIMS used in EMNLab. Important components of the instrument are labeled.
Time-of-flight SIMS utilizes a rastered, pulsed, primary analysis beam, rather than the continuous beam used in other SIMS instruments. Analysis is typically performed with a 15 or 25 keV $^{69}$Ga source. Since the source is isotopically pure, $^{69}$Ga atoms from the analysis beam may be distinguished from Ga lattice atoms by monitoring $^{71}$Ga, which exists in ~40% isotopic abundance.

Secondary ions ejected from the analysis surface are electrostatically accelerated into a drift region, where the flight time $t$ from the sample to the detector is given by:

$$ t = \frac{L_0}{v} = L_0 \sqrt{\frac{m}{2eV_o}} \quad (2.10) $$

In Equation (2.10), $V_o$ is the accelerating voltage, $m$ is the particle mass, $e$ its charge, $v$ its velocity, and $L_0$ the length of the mass spectrometer. The pulsed Ga$^+$ beam can be interlaced with either an O$_2^+$ or Cs$^+$ sputter beam, which tends to enhance cation and anion detection respectively according to Figure 2.10. Ejected ions pass pre- and post-spectrometer blankers which improve trace ion yields by selectively blanking user-designated ions that can saturate the detector. Secondary electrons are diverted to a secondary electron detector (SED) so that an SEM image of the analysis surface can be utilized for positioning. A series of electrostatic lenses guide the secondary ion beam to the detector where the masses of ionized species are resolved by flight time according to Equation (2.10). For depth profiling, the Ga$^+$ analysis beam is rastered over a small area in the center of the sputter crater (typically 20 µm versus a 400 µm crater). The large difference in analysis and sputter beam raster areas is necessary to avoid crater edge effects which result in artificial interface smearing. SIMS imaging, which produces
two-dimensional elemental maps of a structure, is also possible. For the analysis of insulators, where sample charging can modify the analysis beam distribution, a 20 eV electron flood gun is used to compensate charges between analysis beam pulses.

Time-of-flight (TOF) SIMS offers a number of advantages over other SIMS such as quadrupole and magnetic sector instruments. The parallel detection capability of TOF SIMS allows for the simultaneous collection of data from a wide range of masses with high signal-to-noise ratio. Alternative SIMS techniques scan the entire mass range to record a spectrum, examining one small mass range per unit time. This can result in a loss of information and makes elemental imaging more difficult and time consuming. Additionally, the inherently pulsed nature of the TOF SIMS analysis beam allows for attractive features such as a charge compensation phase for insulator analysis.
CHAPTER 3

THE LATTICE-MATCHED INGAAS/INP HETEROJUNCTION

3.1 Sample Structure

The structures used in this study are five nominally \((n \approx 10^{15} \text{cm}^{-3})\) undoped, lattice-matched, InP/In\(_{0.53}\)Ga\(_{0.47}\)As/InP double heterostructures (DHs) grown on semi-insulating Fe-doped (100) InP substrates with no \((\pm 0.2^\circ)\) miscut by solid source MBE with valved cracker sources for arsenic and phosphorus. Prior to being loaded into the growth chamber, epi-ready InP wafers are subject to a 60 min. 300\(^\circ\)C anneal under a pressure of 5x10\(^{-9}\) torr to remove water vapor. Substrate oxide desorption is done in the growth chamber at a temperature of 510\(^\circ\)C under a P overpressure of 1x10\(^{-5}\) torr. The observed \((2x4)\) reflection high energy electron diffraction (RHEED) pattern indicates a clean (100) InP surface. After oxide desorption, growth takes place at 485\(^\circ\)C using Group-V to Group-III beam pressure ratios of 24:1 for InGaAs and 12:1 for InP. Growth rates are 1.743 and 3.180 \(\text{Å/s}\) for InP and InGaAs respectively. Figure 3.1 shows a growth diagram for the five DHs. Beginning at the substrate, the layers are: 200 nm InP, 500 nm In\(_{0.53}\)Ga\(_{0.47}\)As, and 50 nm InP. Arsenic soak times at the InGaAs-on-InP interface, defined as the length of time that As is allowed to soak on the 200 nm InP surface after the P source is closed and prior to InGaAs growth, are 20, 60, 90, 120, and 150s for the five respective structures. A \((2x4)\)-fold RHEED pattern remains stable during As\(_2\)
exposure on the 200 nm InP layer for all five structures. This indicates consistent conditions for the growth of subsequent layers. Growth at the InP-on-InGaP interface is identical for all five samples. Prior to any analysis, the five different 2” diameter wafers are cleaved \textit{ex-situ} to yield samples of approximately 0.25 cm$^2$.

![Figure 3.1: Growth diagram for InP/In$_{0.53}$Ga$_{0.47}$As/InP DHs with a variable As soak at the InGaAs-on-InP interface. Time increases from left to right.](image)

Figure 3.1: Growth diagram for InP/In$_{0.53}$Ga$_{0.47}$As/InP DHs with a variable As soak at the InGaAs-on-InP interface. Time increases from left to right.
Figure 3.2 displays the finished structures. Both control and variable interfaces are labeled.

Figure 3.2: Picture of the InP/In$_{0.53}$Ga$_{0.47}$As/InP DHs studied. The InGaAs-on-InP interface is subject to a variable (20-150s) As soak during growth. The InP-on-InGaAs interface has a constant 20s P soak and acts as a control.

3.2 Analysis of Growth Diffused Junctions

3.2.1 SIMS Analysis

In order to quantify the effects of diffusion related to the extended As-soak, negative-ion secondary ion mass spectrometry (SIMS) is performed on a PHI TRIFT-III TOF SIMS with a background pressure during analysis of 2x10$^{-9}$ torr. For depth profiling, a 1 keV Cs$^+$ beam is used as a sputter source. The analysis beam is a 15 keV focused $^{69}$Ga ion beam. Under these beam conditions, SIMS depth resolution is approximately 3 nm. Typical depth profiling time is 1 hour/sample. The sputter depth rates vary by up to 50% from profile to profile. In order to compare these profiles of intensity vs. sputter depth, the depth scales are normalized the to the beginning of the As
profile decrease at the InGaAs-on-InP interface. These normalized profiles provide a relative measure of interface broadening.

Figure 3.3 shows SIMS As depth profiles for structures exposed to 20 and 150s As soaks at the InGaAs-on-InP interface. InGaAs-on-InP interfacial broadening for 150s As soak relative to 20s As soak is clearly identified.

As and P profiles for all five structures and both interfaces are shown in Figure 3.4. Arsenic and P profiles broaden with increasing As soak time at the InGaAs-on-InP interface. No difference in interface width is observed at the InP-on-InGaAs control interface.
Figure 3.4: C\textsuperscript{+} SIMS As and P depth profiles for all five structures, shown at the (variable soak) InGaAs-on-InP interface and the (control) InP-on-InGaAs interface. An extended As soak leads to broadened InGaAs-on-InP interface profiles, while the control interface is similarly abrupt in all five structures.

It is assumed that the structure with a 20s As soak time at the InGaAs-on-InP interface is atomically abrupt, and that the observed ~8.5 nm broadening is a result of the sputter process at the 550 nm profiling depth. The interface width is defined as the distance over which the SIMS-measured As intensity changes from 90 to 10% of its InGaAs epilayer...
value. The interface widths obtained from both As and P profiles are demonstrated graphically in Figure 3.5 which shows that, with the exception of the 90s outlier, an increase in As soak time monotonically broadens the InGaAs-on-InP interface width.

Figure 3.5: Cs⁺ SIMS As and P profile 90-10% widths. An 8 nm increase in interfacial broadening is observed as the As soak time at the InGaAs-on-InP interface increases from 20 to 150s. The width of the InP-on-InGaAs control interface is a constant ~7.5 nm.

Figure 3.5 demonstrates ~8 nm InGaAs-on-InP interface broadening in 150s soaked structure relative to the structure with 20s As soak. All profiles are abrupt at the InP-on-InGaAs control interface to within the ~7.5 nm sputter-induced broadening of the SIMS at the 50 nm profiling depth. No saturation in As diffusion is observed in Figure 3.5 for As soak times up to 150s (i.e., the interface width continues to increase with increasing As soak time).
3.2.2 Ga-P Fragment Detection

The SIMS process results in the ejection of not only elemental species but also fragments of molecular complexes. Such fragments may indicate local chemical bonding as a function of sputter depth. SIMS reveals Ga-P bonds at both the InGaAs-on-InP and InP-on-InGaAs interfaces. Recombination with the $^{69}$Ga SIMS analysis beam is ruled out by restricting the analysis to $^{71}$Ga-P species (denoted Ga-P through the remainder of this thesis). Figure 3.6 shows the Ga-P, As, and P SIMS profiles as a function of InGaAs-on-InP interface soak time. Ga-P bonding occurs at the InGaAs-on-InP interface in all five samples, and extends into InP as much as 11 nm. In the samples exposed to 20-90s As soak, the Ga-P profile at the InGaAs-on-InP interface tends to extend deeper than the As profile. This is in contrast to the structures with 120 and 150s As soak time, where the InGaAs-on-InP interface Ga-P profile tends to be shallower than the As profile. While this could be due to a change in the relative sensitivity factors for the elements of interest, it is noted that the ratio of As to Ga-P is similar in, for instance, the 20 and 150s soaked structures, and that the 150s Ga-P feature is still more shallow than the 20s Ga-P feature relative to their respective As profiles; therefore, a shallower Ga-P profile with longer As soak times at the InGaAs-on-InP interface is likely to be accurate. Ga-P behavior at the InP-on-InGaAs control interface is similar in all five structures.
Figure 3.6: Raw Cs⁺ SIMS As, P, and Ga-P profiles for all five structures. Structures with 20-90s As soak exhibit Ga-P bonding at the InGaAs-on-InP interface which extends deeper relative to As than Ga-P bonding in structures with 120-150s As soak. Ga-P behavior at the InP-on-InGaAs interface is similar in all five structures.
Figure 3.7 shows the integrated intensity of Ga-P bonding at the InGaAs-on-InP interface relative to the InP-on-InGaAs interface, as a function of InGaAs-on-InP interface As soak time. Since InP-on-InGaAs interface growth is constant for all five structures, the Ga-P intensity at this interface serves as a control by which to measure changes in Ga-P bonding at the variable soak, InGaAs-on-InP interface. In the most abrupt structure, subject to a 20s InGaAs-on-InP interface As soak, approximately 2X the amount of Ga-P bonding is observed at the InGaAs-on-InP interface relative to the InP-on-InGaAs interface. Ga-P bonding at the InGaAs-on-InP increases approximately 25%, to ~2.5X the InP-on-InGaAs interface level, as the As soak time is increased from 20 to 150s. The increase in Ga-P bonding is evident with As soak times as short as 60s.

Figure 3.7: Ratio of InGaAs-on-InP to InP-on-InGaAs Ga-P bonding intensity. A 20-25% increase in Ga-P bonding is observed in structures with 120 and 150s As soak at the InGaAs-on-InP interface, relative to the 20s structure.
3.2.3 AFM Measurements

In order to identify the effects that an extended As soak at the InGaAs-on-InP interface has on surface morphology, atomic force microscopy (AFM) is performed on a Veeco Dimension 3100. AFM measures surface topography on a sub-nanometer scale by optically measuring the deflection of a cantilever by surface forces. This measurement of surface topography is demonstrated in Figure 3.8.

Tapping mode, in which the cantilever tip makes intermittent contact with the sample, is used for these measurements. AFM images, shown in Figure 3.9 for samples with 20 and 90s InGaAs-on-InP interface As soak time, show step-flow growth and Å-scale root
mean square (RMS) roughness. Figure 3.10 shows RMS roughness versus InGaAs-on-InP interface As soak time. Multiple spots are analyzed for each sample and averaged to determine the σ error bars. A 40% increase in RMS roughness is observed with increasing As soak time at the InGaAs-on-InP interface.

Figure 3.9: Representative AFM images for structures with 20s (left) and 90s (right) As soak at the InGaAs-on-InP interface. All structures demonstrate step-flow growth.
Figure 3.10: AFM-measured RMS roughness versus InGaAs-on-InP interface As soak time for all five structures. While all structures are rough on only an Å scale, a 40% increase in RMS roughness is observed for an As soak time of 150s relative to the most abrupt, 20s soaked structure. Error bars correspond to one standard deviation from the mean of multiple measurements.

3.2.4 Cathodoluminescence Data

CLS is performed using a JEOL JAMP-7800F UHV scanning electron microscope (SEM) as the electron-beam source. Emissions are measured using an Edinburgh Instruments high-purity germanium (HPGE) detector. Measurements are at 10 K in cross-section (XCLS) with a beam energy and current of 5 keV and 1 nA respectively. Monte Carlo simulations similar to those shown for GaAs (Figure 2.3) demonstrate that approximately 90% of electron energy is given up within 60 nm of the incident beam. XCLS allows for the accurate positioning of a high resolution beam without the beam spreading and self-absorption effects that accompany a higher energy beam necessary to reach deep interfaces in plan-view analysis. To actively excite the
InGaAs-on-InP interface in plan-view requires a beam energy $E_b \sim 15$ keV. A beam of this energy exhibits significant spreading and, correspondingly, little ability to depth-resolve electronic features. A comparison which demonstrates the benefit of cross-sectional versus plan-view CLS analysis for deep interfaces is shown in Figure 3.11.

![90% of XCLS Electron Energy Loss](image)

Figure 3.11: A comparison of plan-view versus cross-sectional electron energy loss for probing deep interfaces. A CASINO analysis demonstrates that 90% of XCLS energy loss is within 60 nm of the 550 nm deep InGaAs-on-InP interface. This is contrasted with a 15 kV plan-view CASINO simulation showing a distribution extending over 1 µm into the structure.\textsuperscript{120}
XCLS spectra, shown in Figure 3.12 as a function of the distance from the InP-vacuum interface, as well as InGaAs-on-InP interface As soak time, provide a measure of electronic changes due to the observed SIMS diffusion and chemical bonding. The InGaAs emission is the focus of this study as recombination in this layer is highly efficient: a CLS signal from the 50 nm InP cap can not be obtained due to carriers diffusing and recombining outside of this region. XCLS signals from the InP buffer layer are only apparent at distances of ~500 nm from the active InGaAs layer. This is partially due to the low signal intensity for both the HPGE detector and PMT in the ~1.4 eV range.

Figure 3.12: XCLS spectra showing InGaAs emission as a function of distance from the InP-vacuum interface. Structures with the longest InGaAs-on-InP interface As soak time exhibit two features.
InGaAs NBE emission shows one dominant feature for the structures with 60 and 90s As soak time at the InGaAs-on-InP interface. Spectra for structures with 120 and 150s As soak can be deconvolved into two features. Emission energies are relatively similar for all but the 120s soaked sample, which is lower by ~10 meV. This could be due to a small (~1%) variation in mole fraction in this structure. If the deconvolved features are plotted versus position, demonstrated in Figure 3.13, it is clear that while one feature behaves as expected, peaking in intensity close to the middle of the InGaAs layer. The other, lower energy feature, increases towards the vacuum. The feature increases for several hundred nanometers into the vacuum and is visible microns from the interface. The increase of the lower energy feature into the vacuum is explained by Figure 3.14, which shows how the front surface of the structure can be excited by a beam not incident on the sample due to the beam focal point still being in the plane of the cross-sectional surface.
Figure 3.13: Deconvolved cross-sectional InGaAs feature area versus position. The lower energy peak, shown in red, increases in intensity towards the vacuum. The higher energy peak (black) is maximized near the middle of the InGaAs layer.
Figure 3.14: Pictorial description of how a beam focused off of the cross-sectional surface can excite the plan-view face of the structure. If the free surface is close enough to the beam, the sample surface can be excited directly by the beam spreading beyond the focal point. If the sample surface is farther away, then scattered electrons from the mounting block can excite the surface.

3.2.5 SET Measurements

A JEOL JAMP-7800F UHV scanning electron microscope (SEM) is used to measure secondary electron thresholds (SETs) and, correspondingly, work function changes across the cross sectional InGaAs-on-InP interface. These measurements are described in Section 2.5. In this study, a -12 V bias is applied to the sample so that emitted electrons of all energies are collected by the hemispherical analyzer; therefore, the energy onset in Equation (2.9) represents the difference in semiconductor and
analyzer work function, plus a 12 eV offset. Changes in the surface Fermi-level position due to contamination or pinning will change the local SET measurement. To ensure a clean, unpinned, \{110\} surface, heterostructures are cleaved \textit{in-situ}. Structures that show evidence of cleave-related defects in the region of interest under SEM imaging are discarded. Primary electrons have energy 5 keV with an electron beam current of 1 nA. At the X80,000 SEM magnification used for these measurements beam-positioning resolution is approximately 50 nm. This is small relative to the micron-scale space charge regions in these nominally undoped structures. In a semiconducting sample, the bias and analyzer work function remain constant while the semiconductor work function changes with $E_F$ position in the band-gap. Therefore, SETs measure the semiconductor vacuum-level position $E_{\text{vac}}$ with a constant offset. Subtracting literature values for InGaAs and InP electron affinities (which are assumed to be constant in the respective semiconductor materials) from the $E_{\text{vac}}$ data yields the conduction-band edge in the region of electron beam excitation, with a constant offset due to the applied voltage and analyzer work function.

Figure 3.15 shows an SEM image of an in-situ cleaved structure with analysis positions on a line angled to the interface. Also shown is the result of a single SET measurement with the linear onset extrapolated to the baseline to determine $\Delta E$ of Equation (2.9). The square points on the SEM image denote the set of measurement positions for a single profile. Similar profiles are collected across the InGaAs-on-InP interface at several positions for each structure. Each set of measurements requires approximately 20 minutes. Auger electron spectroscopy (AES) verifies the absence of
oxygen and carbon to within its resolution limit (~1%) before and after each series of measurements.

Figure 3.15: SEM image (left) showing analysis points for a series of SET measurements taken across the {110} InGaAs-on-InP interface. The result of a single analysis point is shown on the right, where the extrapolation of the leading edge to the baseline gives $\Delta E$ in Equation (2.9).

Figure 3.16 displays one representative set of cross-sectional SET measurements for each of the five structures (soak times). Energy error bars are calculated from the intersection of the $2\sigma$ confidence bands with the baseline; therefore, error bars vary according to the strength of the linear fit for each measurement. Figure 2.8 shows that, under the beam conditions used, ~95% of secondary electrons are ejected from the surface within 130 nm of the incident electron beam. This determines the “interface region” corresponding to the shaded area of Figure 3.16. The change in SET as the primary electron beam is moved from InGaAs into InP corresponds to the change in $E_{\text{vac}}$ relative to $E_F$ (i.e., the semiconductor work function $\Phi_s$) across the interface region. The
set of SET profiles indicates that the change in $\Phi_s$ from InGaAs-to-InP decreases with increasing As soak time, with the change occurring primarily across the interface region.

Figure 3.16: SET measurements at positions across the *in-situ* cleaved InGaAs-on-InP interface. SET data is shown as a function of InGaAs-on-InP interface soak time. The change in SET across the “interface region” decreases in the InGaAs-to-InP direction as interface As soak time increases.

Figure 3.17 summarizes the change in SET across the InGaAs-on-InP interface region as a function of interface As soak time. Each data point represents an average of the SET-measured change across the interface region at multiple positions on the {110} face of each structure. The change in SET and the associated error bars are averaged,
with each data point assigned unity weight, to obtain the error bars shown. Figure 3.17 shows that the average SET measured from InGaAs into InP increases by $80\pm30$ meV for the most abrupt structure with a 20s As soak. On the other hand, the SET decreases by $130\pm30$ meV for the most diffused structure with a 150s soak. The SETs exhibit intermediate changes between these two soak time extrema. Figure 3.17 demonstrates a near-monotonic, almost linear, relationship between As soak time and change in SET across the InGaAs-on-InP interface. A total change of $-210\pm40$ meV is observed between samples with 20 and 150s As soak time.

![Graph](image)

**Figure 3.17**: Total change in SET versus electron beam position across the InGaAs-on-InP interface region. The change is from InGaAs into InP versus As soak time. The dashed line corresponds to zero change.
3.3 Analysis of Annealed InGaAs/InP DHs

3.3.1 Experimental Setup

After initial analysis, samples are annealed at temperatures of 440, 460, and 495°C for 3000s in ultra-high vacuum (UHV). Anneal temperatures are measured by an E2T Pulsar II 7000EH-2 optical pyrometer focused through a quartz window onto a Mo sample mount. Since quartz is absorptive in the IR range used by the pyrometer, it is calibrated versus sapphire readings to obtain accurate temperature measurements. For accurate anneal-time measurements it is important to verify that the warming and cooling time of the sample mount is short relative to the anneal time. The cooling process may be modeled with Newton’s Law of Cooling, written below:

\[
T(t) = T_{\text{ambient}} + (T_0 - T_{\text{ambient}})e^{-rt}
\]  

(3.1)

The principle is that an object heated to \(T_0\) will approach the ambient temperature \(T_{\text{ambient}}\) by exponential decay with rate constant \(r\). The radiative cooling time constant (\(r^{-1}\)) of the heating mount used in this study is 98s, indicating fast cooling relative to the 3000s anneal time. A measure of the cooling time constant of the sample mount, as well as the pressure during annealing, is shown in Figure 3.18.
Figure 3.18: Heating mount response to heating and cooling in UHV. Fast heating and cooling cycles relative to the 3000s anneal time are demonstrated.

Chamber background pressure while annealing, shown in Figure 3.18, is \( \sim 5 \times 10^{-8} \) torr. The UHV annealing condition, by the Schottky processes listed in Equation (1.14), results in the enhanced desorption of Group-V elements from the surface. This desorption leads to an enhancement of the in-diffusion of vacancies which influences the diffusion process. At the extreme, this in-diffusion can be high enough to disturb the stoichiometry of the sample and result in surface degradation. Temperatures are kept low to minimize this Group-V out-diffusion and any corresponding surface degradation.
3.3.2 SIMS Analysis of Annealed Junctions

Figure 3.19 shows the As and P profiles of samples with 90s As soak time at the InGaAs-on-InP interface after 3000s UHV anneals at 440, 460, and 495°C. The profiles exhibit monotonic InGaAs-on-InP interface broadening from ~8-60 nm with annealing. This broadening is demonstrated graphically in Figure 3.20.

![Graph showing SIMS depth profiles of InGaAs-on-InP interface after annealing for 3000s in UHV at 440, 460, and 495°C.](image)

Figure 3.19: InGaAs-on-InP interface As and P Cs⁺ SIMS depth profiles after annealing for 3000s in UHV at 440, 460, and 495°C. Annealing results in transition region broadening from ~8-60 nm.
Figure 3.20: Cs⁺ SIMS As and P profile 90-10% widths. As and P track closely and overlap at some points. A monotonic increase in interfacial broadening is observed with increasing anneal temperature.

An activation energy and diffusion coefficient can be extracted from the annealed-structure SIMS profiles. Assuming a Fickian model, the solution to Equation (1.9) with initial boundary conditions corresponding to a constant As surface concentration of half its bulk value $C_0$ is given by Equation (3.2).

$$C(z,t) = \frac{C_0}{2} \left(1 - \text{erf} \left(\frac{z}{2\sqrt{Dt}}\right)\right)$$  \hspace{1cm} (3.2)

The assumption of Fickian diffusion is normally only valid in an isotropic lattice and must be qualified; however, Fick’s law has been found to accurately model diffusion on the Group-V sublattice in In$_{0.66}$Ga$_{0.33}$As/In$_{0.66}$Ga$_{0.33}$As$_{0.7}$P$_{0.3}$ heterostructures.\textsuperscript{87} Lattice
strain can result in non-Fickian diffusion, and has been reported at sub-800°C temperatures in InGaAs/InP quantum wells; however, the thick InGaAs layer used in this study is highly resistant to the changes in lattice strain that occur with differing diffusion rates on the Group-III and Group-V sublattice. Therefore, if a strained layer does form, its effect on diffusion is expected to be minimal. Furthermore, the anneal times used in this study fall in the regime that Bollet et al. attribute to Fickian diffusion.

In order to remove the effects of diffusion related to the elevated growth temperature, as well as knock-on effects due to the SIMS sputter process, the broadening observed in the non-annealed SIMS profile is subtracted from the annealed profiles. This subtraction is demonstrated in Figure 3.21. To aid in the subtraction, curves are subjected to a five point adjacent-averaging smoothing function.

![Graph](image)

**Figure 3.21:** Demonstration of the subtraction of control structure (instrumental) broadening from the annealed structure SIMS profiles.
After subtracting instrumental broadening, the resulting As profiles for the annealed structures are fit to the error function solution of the diffusion equation (Equation 3.2). The subtracted curves and error function fits are shown in Figure 3.22. Figure 3.23 shows the Arrhenius plot from which $E_{\text{act}} = 2.29 \pm 0.13 \text{ eV}$ and $D_0 = 1.45 \text{ cm}^2/\text{s}$ (error bars from 0.18-11.31 cm$^2$/s) are measured.

Figure 3.22: As profiles resulting from subtracting the control structure SIMS broadening from the annealed structure SIMS profiles. These difference curves (solid lines) measure diffusion without sputter-induced broadening. The dashed lines show the error function fits (diffusion equation solution) to these curves.
\[ \ln(D_0) = 0.369 \pm 2.057 \ (D_0 \text{ in } \text{cm}^2) / \text{s} \]

\[ E_{\text{act}} / k_B = 26629 \pm 1511 \text{ K} \]

Figure 3.23: Arrhenius plot used to calculate \( E_{\text{act}} = 2.29 \pm 0.13 \text{ eV} \) and \( D_0 = 1.45 \text{ cm}^2/\text{s} \).

3.3.3 Effects of Annealing on Ga-P bonding

The effect of annealing on the Ga-P fragment profile at the InGaAs-on-InP interface is shown in Figure 3.24. Annealing broadens the Ga-P fragment profile from an initial FWHM of 12 nm to greater than 40 nm. The symmetric shape of the unannealed Ga-P peak in Figure 3.24 indicates that broadening due to knock-on sputtering is minimal.
Figure 3.24: $^{71}$Ga-P SIMS profiles at the InGaAs-on-InP interface in annealed structures. Annealing tends to broaden the Ga-P profiles.

3.4 Discussion

3.4.1 SIMS-Measured Interface Broadening

In samples with an extended As soak at the InGaAs-on-InP interface, the observation of As at depths exceeding the few monolayers over which As-P exchange is reported to occur indicates that the observed 8 nm broadening is due to the diffusion of As into the InP buffer layer, forming InAsP. The activation energy of the As-P exchange reaction is reported to be 1.2-1.7 eV, the scatter in these values likely owing to differences in growth conditions.$^{9,10,140,141}$ As discussed in Section 1.3, factors such as
chamber memory effects (determined by volume and pumping speed among other variables) and beam pressure ratios affect the desorption of P atoms, as well as the subsequent incorporation of vaporous As into the InP lattice. This out-diffusion of P atoms explains the P profile broadening in the SIMS profiles in Figure 3.4.

It is important to keep distinct the diffusion processes that occur during and after interface growth. After interface growth, point-defect concentrations are well established and more bonds may need to be broken for diffusion to proceed. Due to a number of different annealing conditions, activation energies vary widely for anneal-induced diffusion at InGaAs/InP junctions. The 2.16-2.42 eV activation energy window derived here from annealing in UHV is at the lower end of the 1.7-5.8 eV reported.\textsuperscript{82,106,107} This is not surprising due to the UHV annealing condition, under which diffusion should proceed particularly rapidly. Specifically, this is because UHV anneals are expected to introduce significantly more vacancies (which generally enhance diffusion) than anneals performed under higher background pressures. Indeed, that significant diffusion is observed in this study at anneal temperatures less than $T_{\text{growth}}$ is indicative of this. Because of this particularly rapid diffusion, the $E_{\text{act}}$ derived here may serve as a lower bound for the diffusion process. The production of P vacancies in a bulk crystal has an activation energy of approximately 2.0.\textsuperscript{82,87,142} It is reported that diffusion in InGaAs/InP proceeds via both grown-in defects and those created by annealing, leading to a two-stage Fickian process.\textsuperscript{87} The UHV annealing condition enhances surface vacancy creation. This enhancement results in a larger supply of vacancies to the crystal, leading to a diffusion process that proceeds via both grown-in and created point-defects, with a lower
activation energy than that a process that requires both the creation of, and subsequent movement through, bulk vacancies.

A potential source of error in this calculation is in the assumption of a constant As “surface” concentration in Equation (3.2). This assumption requires that the 50% As-P crossover point remains at a constant depth. In fact, only small (~5 nm) movements of this crossover point are observed relative to the Ga-P peak position (which serves as an interface marker) after annealing. This indicates that the assumption of a constant 50% As surface concentration is reasonable. The temperature-dependent diffusion coefficient $D(T)$ measured here is found to differ significantly from that reported by Bollet et al. when extrapolated to higher temperatures ($2.4 \times 10^{-11}$ cm$^2$/s versus $4 \times 10^{-14}$ cm$^2$/s at 800°C).\textsuperscript{82} Differing diffusion mechanisms or competing processes could be present due to the large difference in anneal temperature and sample structure (500 nm versus 10 nm respective InGaAs layers), as well as the differences in annealing conditions. Additionally, since the temperature-independent prefactor is determined by the y-intercept of the plot in Figure 3.23, and the temperatures used here are closely grouped far from the y-axis, a large error in $D_0$ is expected. Annealing in vacuum precludes the use of higher temperatures in order to maintain sample stoichiometry and surface integrity. Indeed, minor surface degradation is observed in the InGaAs/InP structure annealed at 495°C. The beginning of a concentration dependence might be evident in the long “tail” of the SIMS profile for this structure, shown in Figure 3.19.
3.4.2 Ga-P Bonding

Figure 3.6 shows InGaAs-on-InP interface Ga-P bonding that occurs at a greater depth than As containing fragments in the non-annealed structures with 20-90s As soak time. These Ga-P bonds indicate that Ga is competing for P-bonding early in interface growth. The increase in Ga-P bonding with As soak time, demonstrated in Figure 3.7, shows that the width of the interfacial InAsP layer produced by As exposure does not preclude Ga-P bonding; instead, it counter-intuitively enhances it. That Ga is able to compete with In for P-bonding is consistent with the higher thermodynamic stability of Ga-P (-1.114 eV/molecule.) vs. In-P (-0.78 eV/molecule.). It is shown in Figure 3.6 that As is observed at greater depths than Ga-P bonding at the InGaAs-on-InP interface in structures with 120 and 150s As soak time. The extent of the InAsP interfacial layer created by As diffusion likely precludes significant Ga-P bonding in these structures once the Ga source is opened. Therefore, in order to bond with Ga, P must be diffusing from the underlying InP layer towards the growth surface. This is consistent with Figure 3.7, which demonstrates that an extended anion soak, known from SIMS to broaden the width of the InGaAs-on-InP transition region, increases Ga-P bonding at the same interface. It is likely that vaporous As diffusion and incorporation into the just-grown InP surface, which introduces a mixed-anion InAsP lattice beyond the initial several monolayer coverage, lowers the barrier for subsequent P diffusion. The observation by several authors of P incorporation into InGaAs at InP/InGaAs interfaces is consistent with this explanation.\textsuperscript{20,21} Alternatively, some roughening or island formation might result in a greater surface area over which Ga can bond with P. While this might result in an increased Ga-P signal, it is known from AFM measurements that any increase in
roughening is small, and that step-flow growth is maintained; therefore, three-
dimensional growth at this interface is unlikely. Additionally, a stable and consistent
(2x4)-fold RHEED pattern strongly suggests that growth remains two-dimensional.
Given these considerations, the most likely scenario is that the slow diffusion of As
atoms by a Frank-Turnbull mechanism, beyond the region over which As-P exchange
occurs, forms a mixed-anion InAsP layer that enhances further P diffusion and the
formation of Ga-P bonds.

InAs has a 3.2% lattice mismatch with InP. The thickness that a strained
(pseudomorphic) layer is able to form over without resulting in dislocation formation is
known as the critical thickness \( h_c \), and is given below with the lattice mismatch \( f \):

\[
 h_c = \frac{a_0 \left(1 - \frac{v_{PR}}{4}\right) \left\lfloor \ln \left(\frac{h_c \sqrt{2}}{a_0} + 1\right) \right\rfloor}{2\sqrt{2\pi}f(1 + v_{PR})} \quad (3.3)
\]

\[
 f = \frac{a_0 - a}{a} \quad (3.4)
\]

The lattice constant of the overlayer is \( a \), \( a_0 \) is the lattice constant of the substrate, and \( v_{PR} \)
the Poisson ratio which depends on elastic constants and is \( \sim 1/3 \) for the materials of
interest. A plot of \( h_c \) and \( f \) in InAs_xP_1-x-on-InP is shown in Figure 3.25, and puts bounds
on how thick an interfacial layer can be before its relaxation and the formation of
dislocations.
The critical thickness of the InAs$_{0.65}$P$_{0.35}$ layer reported to form at the InGaAs-on-InP interface is ~9 nm, meaning that, at $x = 0.65$, little relaxation will occur with the observed ~8 nm broadening. AFM and RHEED measurements indicate only small changes in the Å-scale RMS roughness with As soak time; therefore, significant strain-induced dislocation formation does not occur. This, along with the 8 nm SIMS-observed transition region in the most diffused structure, dictates that a homogeneous InAs$_x$P$_{1-x}$ interfacial layer has mole fraction $x \leq 0.7$, though a graded layer (more likely to form) can have a higher mole fraction towards the InGaAs side of the transition region and not relax.
The similar Ga-P bonding profiles observed at the InP-on-InGaAs interface in Figure 3.6 indicate that similar interfacial reactions occur at this interface in all five structures. The mechanism for Ga-P bonding at the InP-on-InGaAs interface may be the replacement of As by P, which is energetically slightly favorable (0.18 eV/molecule for In-P relative to In-As, and 0.34 eV/molecule for Ga-P versus Ga-As) to the replacement of P by As. Indeed, authors observe As-P exchange reactions at both interfaces, forming InAsP and InGaAsP layers at the InGaAs-on-InP and InP-on-InGaAs interfaces respectively.

3.4.3 CLS Measurements

The CL results in Figure 3.12 are generally consistent with the chemical analysis provided by SIMS. The band-gap of InGaAs lattice-matched to InP is measured by photoreflectance to be 0.807 eV at 10K. A slightly lower emission of approximately 0.79 eV is observed here and is probably due to NBE transitions. The interfacial Ga-P fragments demonstrated in SIMS depth profiles indicate compositional changes at both the InP-on-InGaAs and InGaAs-on-InP interfaces. The CLS observation of a lower energy feature that is dominant near the InP-on-InGaAs interface is curious since it is known from SIMS that the interface structure here is similar. A decrease in this feature towards the InGaAs-on-InP interface, particularly in the samples with the longest 120 and 150s interface soaks, could be indicative of a parasitic interfacial layer that quenches a bulk emission in these structures. The data supports no systematic correlation between peak energy and As soak time. It is unlikely that a thin interfacial layer of the composition that might form here can be detected by CLS. This is because higher $E_g$
interfacial layers with no confinement tend to have very low recombination efficiencies (i.e., carriers formed in a higher $E_g$ interfacial layer are swept to the lower energy InGaAs layer and recombine there). A lower $E_g$ interfacial layer likely emits below the $\sim 0.75$ eV detection limit of the HPGE detector.

3.4.4 SET Measurements

SET measurements probe electronic band structure changes associated with the SIMS-measured broadening at the InGaAs-on-InP interface. The measured $E_{\text{vac}} - \chi$ on each side of the heterojunction yields a conduction-band profile with a constant offset due to the applied bias and analyzer work function. Bulk electron affinity values are: $\chi(\text{InP}) = 4.40$ and, from a Vegard's law interpolation between $\chi(\text{GaAs}) = 4.07$ and $\chi(\text{InAs}) = 4.90$, $\chi(\text{In}_{0.53}\text{Ga}_{0.47}\text{As}) = 4.51$.\(^1\) Figure 3.26 illustrates how $\Delta E_c$ can be extracted from SET data by subtracting $\chi$ on either side of the heterojunction. The $E_c$ profile of Figure 3.26 is calculated from Poisson’s equation (using $\Delta E_c = 0.250$ eV) and is therefore meant as more of a qualitative demonstration than a quantitative one. The band-bending on either side of the heterojunction does, however, bear a striking resemblance to the SET profile shape, as expected.
Figure 3.26: Calculated band diagram and SET data for an abrupt InGaAs-on-InP junction with a 20s As soak at the InGaAs-on-InP interface. The markers on the band diagram correspond to the SET-measured 190 meV change in band position. The experimental results are in good agreement with the known interface conduction band-offset of 250 meV.

It should be noted that this method does not provide a direct measurement of \( \Delta E_c \); rather, \( E_c \) is monitored as it changes relative to \( E_F \) in the space charge region on either side of the heterointerface. This distinction is important: the band-offset at a semiconductor heterointerface is a property of the two intrinsic materials and is maintained by charge compensation on a monolayer-scale around the interface.\(^\text{115}\) The shape of the bands in the interface region after heterointerface formation can be solved for using Poisson’s equation and are governed by the charge transfer which aligns \( E_F \). In the solution of Poisson’s equation, \( \Delta E_c \) enters as a boundary condition. In structures with low doping,
such as the InGaAs/InP samples studied here, the space charge regions are micron-scale and only small changes in $E_c$ are expected over the $\sim 0.1 \mu m$ SET resolution defined by the beam positioning and secondary electron distribution. Therefore, points at the edges of the “interface region” of Figure 3.16 correspond closely to the $E_c$ position directly at either side of the interface, allowing for an approximation of $\Delta E_c$. The $\Delta E_{\text{vac}}$ of $80\pm 30$ meV measured in Figure 3.26 for the abrupt, 20s soaked InGaAs-on-InP interface, corresponds to a $\Delta E_c$ of $190\pm 30$ meV after $\chi$ values are subtracted. This compares favorably with the $\sim 230-250$ meV accepted value. The underestimate in this measurement (190 versus 230-250 meV) is likely due to the resolution limit on how close to the interface $E_c$ data can be obtained; indeed, comparing the SET measurement of $\Delta E_c = 190\pm 30$ meV directly to the known band-offset of 230-250 meV neglects the effects of band-bending. If instead, the change in $E_c$ at the CASINO-predicted resolution limit of the SET technique ($\sim 130$ nm on either side of the interface) is measured from the calculated band diagram in Figure 3.26, a change of $\sim 140$ meV is expected (based on $\Delta E_c = 250$ meV). The 190 meV value obtained via the SET method is therefore an overestimate at the 130 nm distance, possibly owing to a higher SET resolution than that predicted from the CASINO simulation of Figure 2.8. On the calculated band diagram, $E_c$ changes by the experimentally measured 190 meV at a distance of 65 nm on either side of the interface. This 65 nm distance may more accurately reflect the resolution of the technique than the CASINO predictions.

For the most diffused InGaAs-on-InP interface exposed to a 150s As soak, a $\Delta E_{\text{vac}}$ of $-130\pm 30$ meV is measured. Using the procedure outlined above to extract $\Delta E_c$, this
$\Delta E_{\text{vac}}$ corresponds to a $\Delta E_c$ of $-20\pm 30$ meV. Intermediate soak times exhibit intermediate decreases in $\Delta E_{\text{vac}}$ and, correspondingly, $\Delta E_c$. Thus, a decrease in the change in SET across the interface region from InGaAs into InP with increasing InGaAs-on-InP As soak time is consistent with an effective lowering of the conduction band-offset $\Delta E_c$ in these diffused samples.

In the measurement of band structure and band-offset proposed here, the SET curves are expected to “re-converge” at distances far from the interface. This is because at large distances (greater than the space-charge region) bulk film doping rather than interface behavior governs the Fermi-level position and corresponding SET. This expected behavior is shown in Figure 3.27. It is unclear why this re-convergence is not observed in the SET measurements of Figure 3.16. Varying degrees of sample charging in the semi-insulating substrate may account for this disagreement. While the successful measurement of $\Delta E_c$ in the most abrupt structure is a promising indication of the potential of the SET method for approximating band-offsets, more work needs to be performed to refine the technique.
Figure 3.27: Calculated band diagrams for structures with 250 and 0 meV $\Delta E_c$. Far from the interface the conduction and valence bands are expected to reflect bulk conditions.

Such a change in band-offset with interface soak time is not unreported. A decrease in $\Delta E_c$ at InGaP/GaAs interfaces is observed with increasing As soak time.\cite{145} Potentially, a decrease in the effective band-offset can be a result of internal strain, chemical interlayers, interface charges, or defects which alter the interface dipole. Hudait \textit{et al.} present photoconductive decay (PCD) evidence of an As defect-related trap at the InGaAs-on-InP interface, which is associated with long As soak times in these structures.\cite{30} A strained interlayer can also modify the effective band-offset. This change is noted in the InAs$_{1-x}$P$_x$/In$_{0.53}$Ga$_{0.47}$As$_{1-y}$P$_y$ system, where the experimentally measured band-lineup is a function of compositional changes and strain development at the heterointerface.\cite{146} Since several authors report compressively strained InAsP layers or
islands at the InGaAs-on-InP interface, and it is known from SIMS that an InAsP layer is formed by an increased As soak time in these structures, a similar mechanism might alter the band-lineup in InGaAs/InP.\textsuperscript{13,16,147} It is known that InAsP on (100) InP exhibits a (2x4)-fold RHEED pattern similar to (100) InP;\textsuperscript{148} therefore, the stable (2x4)-fold RHEED pattern exhibited during As exposure at the InGaAs-on-InP interface does not preclude the possibility of a strained interlayer.

3.5 The InP-on-InGaAs Interface

3.5.1 Experimental

To complement the previously discussed work on the InGaAs-on-InP interface, three structures with extended P soaks at the InP-on-InGaAs interface are analyzed. Similarly to the previous study, the structures are nominally (n~10\textsuperscript{15} cm\textsuperscript{-3}) undoped, lattice-matched, InP/In\textsubscript{0.53}Ga\textsubscript{0.47}As/InP double heterostructures (DHs) grown by SSMBE on (100) InP (Si-doped) substrates with no (< ± 0.2\textdegree) miscut. An identical pre-growth anneal is performed to remove water vapor. A (2x4) (RHEED) pattern is observed during InGaAs-on-InP interface growth. As is the case with As-soaked structures, during the P soak at the InP-on-InGaAs interface, the RHEED pattern changes to a hazy (3x4) before switching back to a clean (2x4) pattern during growth. Growth takes place at 485\textdegree C using Group-V to Group-III beam pressure ratios of 24:1 for InGaAs and 12:1 for InP. Growth rates are 1.48 and 3.196 Å/s for InP and InGaAs respectively. Figure 3.28 shows a growth diagram for the three DHs, shown pictorially in Figure 3.29. Arsenic
soak times at the InGaAs-on-InP interface are a constant 20s, while the P soak at the InP-on-InGaAs interface is 60, 120, and 150s for the three respective structures.

Figure 3.28: Growth diagram for structures with an extended P soak at the InP-on-InGaAs interface.
Figure 3.29: Picture of the InP/In$_{0.53}$Ga$_{0.47}$As/InP DHs that are the focus of this study. The InGaAs-on-InP interface acts as a control, while the InP-on-InGaAs interface is subjected to a variable P soak during growth.

3.5.2 SIMS Analysis

As and P Cs$^+$ SIMS profiles for structures with 60, 120, and 150s P soak at the InP-on-InGaAs interface are shown in Figure 3.30. A 1 keV Cs$^+$ beam is interlaced with a 15 keV, isotopically pure, focused $^{69}$Ga ion beam (i.e., identical sputter conditions to the diffused InGaAs-on-InP junction analysis). To control for any variation in sputter rate, the depth scales are normalized to the beginning of the As profile decrease from its bulk value at the InGaAs-on-InP interface. The data supports no systematic change in interfacial broadening at either interface, demonstrated graphically in Figure 3.31.
Figure 3.30: Cs\(^+\) SIMS As and P depth profiles for all three structures, shown at the (variable soak) InP-on-InGaAs and (control) InGaAs-on-InP interfaces. An extended P soak does not broaden the profiles.
Figure 3.31: 90-10% interface width at the (variable soak) InP-on-InGaAs and (control) InGaAs-on-InP interface. No systematic correlation between P soak time and interface width is observed.

If the Ga-P bonding observed at the interfaces is integrated, and the ratio of the InP-on-InGaAs to InGaAs-on-InP interface intensity plotted versus P soak time, shown in Figure 3.32, the change with P soak time is only ~4%. This 4% change in Ga-P bonding is significantly less than the 25% change observed in Figure 3.7 at the As soaked InGaAs-on-InP interface, and is likely within the error of the measurement. It is also noted, with reference to Figure 3.33, that the Ga-P bonding profiles at both interfaces show a similar behavior to the 20, 60, and 90s As soaked samples in Figure 3.6; that is, Ga-P bonding at the InGaAs-on-InP interface tends to occur more deeply than the As profile extends, and Ga-P bonding at the InP-on-InGaAs interface tends to occur at a more shallow depth than the P profile.
Figure 3.32: Integrated $^{71}$Ga-P at the InP-on-InGaAs interface relative to the InGaAs-on-InP interface. While a decrease is observed, it is only ~4%. This is contrasted with the 25% change in Ga-P bonding observed with a varying As soak at the InGaAs-on-InP interface, demonstrated in Figure 3.7.
Figure 3.33: Raw Cs⁺ SIMS As, P, and $^{71}$Ga-P for all three structures. Ga-P shows no systematic change in bonding depth versus P soak time, and profiles at both interfaces are similar to the 20-90s As soaked structure profiles shown in Figure 3.6

3.5.3 CLS Analysis

Since the InP-on-InGaAs interface is only 50 nm from the sample surface, plan-view CLS with a variable energy beam provides the highest resolution analysis. CASINO simulations, shown in Figure 3.34, demonstrate the effect of 1-5 keV electron beams on the sample structure studied here. EHP recombination at the InP-on-InGaAs
interface is enhanced by a lack of confinement in the InP layer (i.e., carriers readily diffuse to and recombine in the InGaAs and near-interface region).

Figure 3.34: CASINO simulation of electron distributions around the InP-on-InGaAs interface. Electrons with energies of 3-5 keV directly excite the interface.

Plan-view CLS is performed in the JEOL JAMP-7800F. CLS showing the primary InGaAs emission versus P soak time for all three structures in given in Figure 3.35. The structure with 150s P soak at the InP-on-InGaAs interface exhibits two primary features at $E_b \geq 3$ keV (i.e., in the interface region). The appearance of these two features, at $\sim 0.787$ and $0.792$ eV respectively, could be evidence for compositional rearrangement resulting from the extended P soak time at the InP-on-InGaAs interface;
however, support for this speculation requires additional studies of compositional variation versus P exposure. Otherwise, the data supports no systematic correlation between peak energy and P soak time at the InP-on-InGaAs interface.

Figure 3.35: Plan-view CLS for structures with an extended P soak at the InP-on-InGaAs interface. The incident beam energy is 1-5 kV. The structure exposed to 150s P soak at the InP-on-InGaAs interface exhibits two CLS features for the beam energies > 3 kV which directly excite in the interface region of interest.
3.5.4 Discussion

Little change in SIMS broadening, Ga-P interface bonding, or CLS-measured electronic structure, is observed as a function of P soak time at the InP-on-InGaAs interface. An As-P exchange reaction at this interface is known to form a thin InGaAsP interfacial layer on a ~0.5 nm scale. These results suggest that, after this layer forms, further diffusion of P into the InGaAs layer does not occur. This is supported by no observed increase in InP-on-InGaAs interface Ga-P bonding, as well as identical RHEED behavior, for interface P soak times from 60-150s. While some authors report roughening of the InP-on-InGaAs interface by an extended P soak during GSMBE growth, no evidence of roughening has been observed in this study. It might be that, under the growth conditions used, a low concentration of As vacancies in the InGaAs layer precludes significant P in-diffusion beyond the InGaAsP interfacial layer.

3.6 Conclusions

Systematic differences in diffusion and interfacial compound formation at the InGaAs-on-InP and InP-on-InGaAs interfaces are observed. SIMS depth profiles reveal the presence of nanometer-scale Ga-P bonding at InGaAs-on-InP and InP-on-InGaAs junctions. The position of the Ga-P bonding relative to the As and P profiles indicates that Ga competes favorably versus In for bonding during growth at the InGaAs-on-InP interface. As soak times \( \geq 120\)s broaden the As distribution at the InGaAs-on-InP interface by approximately 8 nm. This broadening results in a shallower, enhanced Ga-P bonding profile as it introduces strained, mixed-anion lattice that enhances P diffusion into the growing InGaAs layer. AFM measurements, as well as a consistent RHEED...
pattern during growth, indicate that no significant interfacial roughening is occurring. These observations, along with a consideration of the critical thickness of a pseudomorphic InAsP layer, set a limit on the width and composition of a strained interfacial layer. XCLS analysis identifies two features close to the InGaAs NBE energy. The higher energy emission behaves as expected, peaking up in the InGaAs layer, while a lower energy emission is dominant away from the InGaAs-on-InP interface and may be indicative of a parasitic interface layer in structures with 120 and 150s InGaAs-on-InP interface As soak time. Using a novel technique in which the secondary electron onset is monitored as an electron beam is scanned across an \textit{in-situ} cleaved \{110\} interface, a \(\sim 190 \pm 30\) meV conduction band-offset is measured at the most abrupt InGaAs-on-InP interface. This measurement agrees well with the 230-250 meV accepted value. Using the same analysis method, a lower \(\Delta E_c\) at the most diffused junction is measured; however, the behavior far from the interfaces is not as expected, possibly due to sample charging. Such an interface change, if not accompanied by added defects or interlayers, can result in lower reverse hole injection in HBTs. Post-growth UHV annealing of these heterojunctions demonstrates the cross-diffusion of As/P on a tens-of-nanometers scale at close to growth temperatures. This diffusion is quantified by SIMS, giving \(E_{\text{act}} = 2.29 \pm 0.13\) eV and \(D_0 = 1.45\) cm\(^2\)/s.

An extended P soak at the InP-on-InGaAs interface produces no systematic change in SIMS broadening or Ga-P bonding. This is consistent with a quick initial replacement of As, after which no significant P in-diffusion occurs. Plan-view CLS reveals two features in the structure exposed to the longest P soak at the InP-on-InGaAs
interface. While this provides some preliminary evidence for a small degree of compositional rearrangement, more work is necessary to verify this speculation.

In general, these interface diffusion and bonding phenomena help define the role of bulk thermodynamics in atomic displacement and exchange reactions at III-V compound heterojunctions in general, and demonstrate that these phenomena have a significant impact on the electronic structure of a lattice-matched III-V heterojunction.
CHAPTER 4

INGAP AND ALINP ON GAAS

4.1 Introduction

It is desirable to extend the chapter three results on the InGaAs/InP junction to other semiconductor systems. In$_{0.49}$Ga$_{0.51}$P and Al$_{0.52}$In$_{0.48}$P have identical Group-V transitions, and similar Group-III transitions (i.e., Al/Ga versus Ga$_{0.51}$/Ga), meaning that similar interfacial reactions are likely at elevated growth or device operation temperatures. These ternary compositions are lattice-matched to GaAs and therefore present model systems for the study of atomic cross-diffusion and associated bulk and interface defect formation at semiconductor heterojunctions, as well as a platform from which to study important issues such as the differences between growing A-on-B, versus B-on-A.

4.2 Structure Growth and Treatment

Structures used in this study are lattice-matched In$_{0.49}$Ga$_{0.51}$P/GaAs/In$_{0.49}$Ga$_{0.51}$P and Al$_{0.52}$In$_{0.48}$P/GaAs/Al$_{0.52}$In$_{0.48}$P double heterostructures (DHs) with low doping (n~7x10$^{16}$ cm$^{-3}$). The epilayers are 500 nm thick, which allows for highly accurate XCLS analysis as carrier diffusion across interfaces is minimized. The DHs are grown on a 200 nm Si-doped (n~4x10$^{18}$ cm$^{-3}$) GaAs buffer layer on N+ (100) GaAs substrates with a 6$^\circ$
miscut by solid source MBE with valved cracker sources for arsenic and phosphorus. A
growth diagram that includes growth temperatures for both InGaP/GaAs and AlInP/GaAs
DHs is shown in Figure 4.1. Figure 4.2 shows a drawing of the two finished structures.

![Growth diagram](image)

Figure 4.1: Growth diagram for InGaP/GaAs (blue/black) and AlInP/GaAs (red/black) DHs showing shutter sequences and growth temperatures.

![DH structures](image)

Figure 4.2: Drawing of the AlInP/GaAs (left) and InGaP/GaAs (right) DHs studied.
Because P tends to desorb from the just-grown InGaP and AlInP layer at high temperatures, it is critical to lower substrate temperatures during ternary growth. Correspondingly, to minimize the formation of \( V_{As} \) during GaAs growth, it is desirable to raise the substrate temperature. These “warm up” and “cool down” cycles are done under Group-V overpressure to minimize Schottky reactions and the corresponding in-diffusion of vacancies. Growth temperatures are 490, 510, and 565\(^\circ\)C for InGaP, AlInP, and GaAs respectively using Group-V to Group-III beam pressure ratios of 9:1 for InGaP, 6:1 for AlInP, and 14:1 for GaAs. Growth rates are 3.175 \( \text{Å/s} \), 3.245 \( \text{Å/s} \), and 1.6165 \( \text{Å/s} \) for InGaP, AlInP, and GaAs respectively. A (2x4)-fold RHEED pattern remains stable during GaAs growth for both structures, indicating consistent conditions for the growth of subsequent layers. To prevent Schottky reactions and the corresponding loss of sample stoichiometry during annealing treatments, samples are capped by 200 nm SiO\(_x\) via electron beam deposition (EBD). Samples are then cleaved and annealed separately for 1 hour in a Lindberg tube furnace under Ar\(_2\) at temperatures from 650\(^\circ\)C-850\(^\circ\)C. Wafer segments are selected for annealing according to Figure 4.3. Control samples are taken from wafer corners. Excellent agreement is found between the control samples, indicating a high degree of wafer uniformity.
Figure 4.3: Structures are cleaved and annealed for 1 hour according to the above diagrams. Segments labeled “C” are not annealed and serve as controls.

4.3 AlInP/GaAs DH

4.3.1 SIMS Analysis of Annealed Junctions

SIMS is performed on a PHI TRIFT-III TOF SIMS with a background pressure during analysis of 2x10^-9 torr. A 5s sputtering cycle with a 3 kV beam is followed by a 3.79s analysis cycle with a 15 kV 69Ga beam. A one second relaxation period between each cycle is used. Typical depth profiling time is approximately 1 hour/sample. Cs^+ and O_2^+ SIMS profiles for control and annealed AlInP/GaAs DHs are shown in Figure 4.4 and Figure 4.5, and measure broadening in anion and cation elements respectively. Significant SIMS diffusion is observed after annealing at T ≥ 800°C in both the anion and cation elements, demonstrated graphically in Figure 4.6 where the 90-10% widths of In, Al, Ga, P, and As, are plotted versus anneal temperature and are normalized to the measured width of the control structure. If the control broadening of ~15 nm is used as a standard, then ~150-300 nm broadening is measured in the most diffused structure. It is
interesting to note the asymmetric broadening at the highest temperatures. Since the
degree of asymmetric broadening observed at $T \geq 800^\circ C$ is significantly greater than that
observed for $T \leq 750^\circ C$, it is possible that this is physical and not an artifact of the sputter
process.

Figure 4.4: Cs$^+$ SIMS depth profiles versus anneal temperature for AlInP/GaAs DHs.
Cs$^+$ sputtering tends to enhance the secondary ion yield of anion species per Figure 2.10.
Approximately 150 nm broadening is observed after the highest temperature anneals.
Figure 4.5: O$_2^+$ SIMS depth profiles versus anneal temperature for AlInP/GaAs DHs. O$_2^+$ sputtering tends to enhance the secondary ion signal of the cation elements per Figure 2.10. Asymmetric broadening is observed beginning at T = 750°C, demonstrating good agreement with the broadening observed in the anion elements in Figure 4.4.
Using the procedure outlined in Section 3.3.2, activation energies can be extracted from these SIMS profiles. There is some variation in SIMS-measured interfacial broadening within the same samples using the 3 kV sputter condition, especially at temperatures $< 750^\circ$C; therefore, there is expected to be some error in the activation
energy measured for As-P cross-diffusion. Diffusion for the metal ions is difficult to accurately analyze quantitatively due to the dramatically different SIMS sputter rates for AlInP and GaAs, as well as significant SIMS knock-on effects for the Group-III elements. An Arrhenius plot for As and P at both interfaces is shown in Figure 4.7.

![Arrhenius plot for As and P diffusion](image)

Figure 4.7: Arrhenius plots used to determine $E_{\text{act}}$ for As and P diffusion at AlInP-on-GaAs and GaAs-on-AlInP interfaces.
The points in Figure 4.7 are not collinear, and appear to consist of high and low-slope components. Both can be fit to obtain activation energies. The activation energies for the high and low-slope regions of the plot are ~7.5-11 eV, and ~0.5-1.5 eV, respectively.

4.3.2 XCLS Analysis

Prior to XCLS analysis, annealed wafers sections are cleaved ex-situ to ensure an analysis surface representative of bulk rather than surface diffusion. Using 10 K XCLS, bulk and interface electronic structure as a function of position and anneal temperature are precisely measured. The low energy (5 kV, 0.5 nA) beam used for this analysis significantly reduces self-absorption and beam spreading. Figure 2.3 shows CASINO simulations for these beam conditions, and demonstrates that approximately 90% of primary electron energy is given up within 60 nm of the incident beam. Since the 5 kV beam penetration is ~100 nm, surface oxide formation resulting from the ex-situ cleave is unimportant. XCLS of AlInP/GaAs as a function of position is demonstrated pictorially, with a set of spectra, in Figure 4.8.
Figure 4.8: Representation of the XCLS technique applied to the study of AlInP/GaAs DHs. CLS performed at the interfaces and in the middle of epitaxial layers yields position-dependent spectra with high resolution, shown on the right.

Several dominant electronic features appear in Figure 4.8. The 2.2-2.3 eV emission corresponds to zero-phonon and (low intensity) phonon transitions from the AlInP X-band. The 1.4-1.5 eV emissions are GaAs transitions corresponding to the ~1.51 eV free exciton, a lower energy ~1.49 eV donor-acceptor (DA) transition, and lower energy phonon-assisted transitions. It is clear that the spectra are sensitive to position: the GaAs-related emissions change from sharp features in the epilayers to broad features indicative of band-tailing as the electron beam excites closer to the degenerately doped substrate. The fact that substrate features are only observed within ~250 nm of the substrate itself demonstrates that the XCLS technique provides a high resolution probe of these structures with little influence from carrier diffusion effects. A low intensity shoulder emission in the ~1.8-2.1 eV region is also apparent. XCLS line scans, shown for some of these emissions in Figure 4.9, are used to spatially localize these features. Line scans performed at 1.98 and 2.27 eV are maximized in the AlInP layers, while the
1.51 eV emission is maximized in the GaAs epilayer and substrate. The lack of spatial dependence to the broad 1.8-2.1 eV AlInP (line scan at 1.98 eV) feature identifies it is a bulk rather than an interface defect. This AlInP-localized emission is consistent with either \( V_p \) at \( E_c-0.65 \text{ eV} \sim 1.92 \text{ eV} \) or O incorporation in the AlInP lattice, with reported energies of \( E_c-0.62 \sim 1.95 \text{ eV} \) and \( E_c-0.85 \sim 1.72 \text{ eV} \).\(^{151,152}\)

![Figure 4.9: CLS line scans performed across cross-sectional interface layers at energies of 1.51, 1.98, and 2.27 eV. These spectra are used to spatially localize the features identified in Figure 4.8.](image)

Figure 4.10 shows the normalized dependence of AlInP features on anneal temperature, as well as a clear picture of the 1.8-2.1 eV shoulder feature. Spectra are for spots taken in the middle of the inner and outer epitaxial AlInP layers. At the 850°C
anneal temperature, the X-band emission is blue-shifted approximately 40 meV from its control value. This is demonstrated graphically in Figure 4.11.

Figure 4.10: CLS spectra taken in the middle of the inner and outer AlInP epilayers. A 40 meV blue shift in the emission energy is noted after annealing at 850°C. The broad shoulder feature is also clearly shown.
Figure 4.11: AlInP X-valley (NP) emission energy versus anneal temperature. A 40 meV increase is observed after the highest temperature anneal.

Once the background level is subtracted off, AlInP features are fit with four Gaussians as shown in Figure 4.12. The ratio of the area of the 1.8-2.1 eV shoulder feature to X-band features increases as a function of anneal temperature, demonstrated graphically in Figure 4.13. The 1.8-2.1 eV feature begins to increase at temperatures as low as 650°C, relatively close to the MBE growth temperature and considerably lower than typical OMVPE growth temperatures. At $T \geq 800^\circ$C the feature shows a relative increase of as much as 5-10X its control value.
Figure 4.12: An example of the Gaussian fitting procedure used to examine AlInP emissions.

Figure 4.13: Integrated ~1.8-2.1 eV feature to AlInP features ratio. The ratio of the intensity of the ~1.8-2.1 eV feature to the three higher energy AlInP features increases with anneal temperature in both the inner and outer AlInP layers.
4.4 InGaP/GaAs DH

4.4.1 SIMS Analysis of Annealed Junctions

Cs$^+$ and O$_2^+$ SIMS profiles for control and annealed InGaP/GaAs DHs are shown in Figure 4.14 and Figure 4.15 respectively. Similarly to the AlInP/GaAs DH, interfaces are relatively abrupt for T $\leq$ 750$^\circ$C and diffuse for T $\geq$ 800$^\circ$C, where broadening of 5-10X the control value of ~26 nm is measured (i.e., ~130-260 nm 90-10% interface width in the most diffused structures). These increases are demonstrated graphically in Figure 4.16.
Figure 4.14: Cs⁺ SIMS of InGaP/GaAs DHs emphasizes anion elements. Like in the AlInP/GaAs DH, structures are abrupt for anneal T ≤ 750°C. 130-260 nm interfacial diffusion is measured for T ≥ 800°C.
Figure 4.15: $O_2^+$ SIMS of InGaP/GaAs DHs emphasizes cation elements. Good agreement with the Cs$^+$ profiles is observed, with broadening at $T \geq 800^\circ C$. 
Figure 4.16: Interface 90-10% width extracted from SIMS profiles of Figure 4.14 and Figure 4.15. The width is normalized to the measured control broadening of ~26 nm.

The process to extract activation energies from SIMS profiles used in Section 3.3.2 is not applicable here as the non-monotonic behavior of the diffusion profiles results in a negative logarithm once the control broadening is subtracted. This non-monotonic behavior is possibly an artifact of the sputtering process, but might also be
related to a slightly inhomogeneous capping layer or metal out-diffusion and vacancy creation during some of the anneals. While this precludes extracting accurate and dependable activation energies from the SIMS profiles, it is evident qualitatively that diffusion under the anneal conditions used is enhanced for $T \geq 800^\circ C$. Literature values of $D_0^\text{In-Ga} = 34 \text{ cm}^2 \text{ sec}^{-1}$, $E_{\text{act}}^\text{In-Ga} = 3.2 \text{ eV}$, $D_0^\text{As-P} = 4 \times 10^{-5} \text{ cm}^2 \text{ sec}^{-1}$, and $E_{\text{act}}^\text{As-P} = 2.38 \text{ eV}$ are reported.\textsuperscript{153}

4.4.2 XCLS Analysis

XCLS as a function of position and anneal temperature, shown in Figure 4.17, reveals several important electronic features: InGaP NBE emission at 1.955 eV, a lower energy ~1.92 eV InGaP emission related to a DA transition,\textsuperscript{154} GaAs NBE and DA emission at 1.51 and 1.49 eV respectively, and, as is the case with AlInP, GaAs emission changes from sharp, easily resolved features to a broad substrate emission as the beam is positioned closer to the substrate layers. At lower energies a broad feature (~1.4 eV) is evident in the semiconductor epilayers; however, this feature is cut-off by the decay of PMT sensitivity in the region and will be discussed with HPGE detector data in the next section. Notably absent from the spectra are $V_P$ observed in the AllnP/GaAs DHs, which are reported to be at $E_c-0.28 \text{ eV}$ (~1.72 eV).\textsuperscript{155}
Figure 4.17: CLS spectra taken as a function of interface position and anneal temperature. InGaP and GaAs features are selectively excited. No $V_p$ are observed at the reported 1.72 eV.
4.4.3 IR-XCLS Analysis of Deep States

Figure 4.18 shows IR-XCLS spectra as a function of position and anneal temperature. A HPGE detector is used for this low energy analysis. Several features are clearly identified: 1.51 and 1.49 eV GaAs NBE and DA transitions, as well as a broad ~1.25-1.45 eV deep feature. The spectral weight of the deep feature increases in energy and decreases in intensity at T = 750°C, and the feature is absent from the T ≥ 800°C spectra. This feature contains considerable substructure which could be indicative of some common GaAs transitions between the different samples; however, attempts to fit Gaussian peaks to the feature show that many of the transitions are not common to the sample set and therefore do not likely describe native GaAs transitions. The 1.49 eV DA transition is observed to increase relative to GaAs NBE after annealing at 750-800°C.
Figure 4.18: IR-CLS shown as a function of interface position (by color) and anneal temperature (by plot). The spectral weight of the ~1.25-1.45 eV emission increases in energy and decreases in intensity after annealing at T ≥ 750°C. A 1.49 eV DA emission also increases in intensity after annealing at 750-800°C.
CLS line scans, shown in Figure 4.19, can be used to examine the spatial dependence of the \(\sim 1.25-1.45\) eV feature. The line scans show that the feature does not track the GaAs emission and is at least an order of magnitude more intense in the 500 nm GaAs epilayer than in the substrate. Both emissions are asymmetric and, while the GaAs emission is maximized towards the InGaP-on-GaAs interface, line scans taken at 1.37 eV, close to the maximum of the broad emission, show that this feature is maximized towards the GaAs-on-InGaP interface; thus, the broad \(\sim 1.25-1.45\) eV emission is an interface-localized feature, and could be parasitic in that it results in a reduction of recombination via the 1.51 eV GaAs NBE route. The asymmetric behavior, particularly with respect to GaAs, occurs for all anneal temperatures where the feature is present (i.e., \(T \leq 750^\circ\text{C}\)). A CLS image further verifying the asymmetric nature of these emissions is shown in Figure 4.20.
Figure 4.19: CLS line scans showing that the broad (~1.37 eV) feature is maximized at the GaAs-on-InGaP interface, while 1.51 eV GaAs NBE emission is maximized at the InGaP-on-GaAs interface. 1.96 eV InGaP NBE emission is maximized in the InGaP layers, as expected. The ratio of the 1.37 eV emission to GaAs is maximized towards the GaAs-on-InGaP interface.
Figure 4.20: XCLS image taken with the JEOL SEM. The image shows the spatial extent of InGaP (green), GaAs (white), and ~1.37 eV defect (red) features. The GaAs and defect features are not symmetrically distributed throughout the GaAs layer, the GaAs being more pronounced at the InGaP-on-GaAs interface and the defect being pronounced at the GaAs-on-InGaP interface. The image confirms the results of Figure 4.19.

The 1.49 eV feature, consistent energetically with a Si acceptor level, also demonstrates interesting behavior by peaking in intensity after annealing at 750-800°C. This behavior is shown in Figure 4.18. Si is amphoteric in GaAs and can form both
acceptor (substitution on a As site) and donor (substitution on a Ga site) levels. To identify the spatial dependence of this feature, it and the 1.51 NBE emission are fit with Gaussians and their ratio examined, as shown in Figure 4.21. The 1.49 eV feature increases relative to GaAs by as much as 3-4X at the interfaces. It should be noted that towards the substrate carrier diffusion and the broad substrate luminescence may artificially enhance this feature. This should, however, be a secondary effect and, given the relatively small amount of carrier diffusion observed, can not account for the considerable change measured here.

![Graph](image)

Figure 4.21: Ratio of 1.49 eV integrated intensity to GaAs NBE integrated intensity. The 1.49 eV feature is maximized relative to GaAs NBE towards the interfaces.
Figure 4.22 shows XCLS spots taken in the middle of the GaAs, inner InGaP, and outer InGaP layers. The behavior of the intensity of these emissions is as expected: GaAs is maximized at the expense of InGaP in the GaAs layers, and InGaP at the expense of GaAs in the InGaP layers. The spectra demonstrate that the InGaP NBE emission blue-shifts after the highest temperature anneals. The 1.51 eV GaAs NBE emission remains constant and acts as a control. This is demonstrated graphically in Figure 4.23, where a ~20 meV shift is evident between the control sample and the structure annealed at 850°C. Additionally, a decrease in the InGaP shoulder emission, which is believed to be a DA transition, is observed in the outermost InGaP layer after annealing at 850°C.
Figure 4.22: CLS spectra taken in the middle of the GaAs, inner, and outer InGaP epilayers. A blue shift in the emission energy is noted after annealing at 800°C. The GaAs emission remains constant and acts as a control.
Figure 4.23: InGaP NBE emission energy versus anneal temperature. A 20 meV blue shift is observed after the highest temperature anneal.

4.5 Discussion

With the exception of the As profile at the GaAs-on-AlInP interface, the points in Figure 4.7 are not collinear. This is similar to that observed by Gillin et al. in the InGaAsP system where the behavior is attributed to two different diffusion mechanisms: one that relies on in-grown vacancies and one that requires the thermal production of vacancies.87 Activation energies for the two processes shown in Figure 4.7 are ~7.5-11 eV and 0.5-1.5 eV. Several authors report activation energies of ~3.6-4.5 eV using the Fickian assumption in PL studies of the Group-III sublattice in AlGaAs/GaAs.109,156-158 It is acknowledged that diffusion in AlInP/GaAs proceeds more slowly; therefore, the
high, 7.5-11 eV activation energy measured here is not necessarily unreasonable. That a higher activation energy process is enhanced relative to a lower energy process at high temperatures means that the diffusion coefficient for the low energy process must be significantly smaller.

A consequence of annealing under an SiO\(_x\) capping layer is that Si in-diffusion can result in IILD; additionally, some Group-III elements, such as Ga, are able to pass through the cap and leave vacancies that can diffuse into the structure and change the diffusion dynamic.\(^{109}\) Significant metal out-diffusion is evident from the SIMS profiles, especially at \(T \geq 800^\circ\text{C}\), and may explain the large amount of diffusion observed at these temperatures; however, both Cs\(^+\) and O\(_2^+\) SIMS show no significant Si incorporation in the inner InGaP and AlInP layers, making significant IILD unlikely.

It is notable that the large CLS blue shifts occur at the same \(\geq 800^\circ\text{C}\) temperatures where SIMS identifies the most significant diffusion. The observed 20 and 40 meV blue shifts in the InGaP NBE and AlInP X-valley emissions respectively can be explained by the cross-diffusion and incorporation of Ga at the expense of In in the ternary lattices. Since the In\(_{1-x}\)Ga\(_x\)P NBE emission is highly sensitive to Ga mole fraction, only a small amount of additional Ga incorporation (~2\%) is necessary to shift \(E_g\) the measured 20 meV. The Al\(_x\)In\(_{1-x}\)P X-band shows considerably less dependence on Ga mole fraction; therefore, the amount of Ga in-diffusion necessary to produce the observed ~40 meV shift is ~25\%.\(^{54}\) These numbers are, however, reasonable given the considerable AlInP interfacial diffusion observed after the 850\(^\circ\text{C}\) anneal where the blue shift occurs (see Figure 4.5). The cross-diffusion of As and P atoms counteracts the effect of Ga and In cross-diffusion on the ternary band-gap (i.e., the cross-incorporation of As and P lowers
the ternary band-gap). Therefore, these Ga incorporation percentages (2 and 25\% for InGaP and AlInP respectively) are lower bounds that assume no As and P cross-diffusion. While As-P cross-diffusion is known to occur from the SIMS profiles of Figure 4.4 and Figure 4.14, the 800\(^{\circ}\)C diffusion coefficient \(D(T)\) measured for In-Ga diffusion is \(~100\times\) greater than that for As-P diffusion (3.2\(\times\)10\(^{-14}\) cm\(^2\)/s versus 2.7\(\times\)10\(^{-16}\) cm\(^2\)/s); therefore, these assumptions are not unreasonable.\(^{153}\) That primarily Ga and In diffuse preferentially to Al is also energetically consistent as the Ga-As and In-P bonds in GaAs and InGaP/AlInP respectively are weak relative to Al-P (0.77 and 0.78 versus 1.703 eV/molecule respectively as shown in Table 1.2). This diffusion (i.e., In preferentially over Al) is not, however, clearly evident from the O\(_2^+\) SIMS data in Figure 4.5 and Figure 4.15, where In and Al track closely. This indicates that the difference in Al and In diffusion is less than the \(~10\) nm resolution of the SIMS under the sputter conditions used.

Another consideration is that some partial ordering could be present in the control structures. While the order parameter \(\eta\) is strongly dependent on growth temperature, being significantly higher in \(~750^{\circ}\)C OMVPE growths, some authors have reported \(\eta\sim0.2-0.3\) in MBE grown material.\(^{61}\) Despite the well-established increase in ordering with growth temperature, ordering is a surface-stable phenomenon and, with annealing, the degree of ordering decreases in both InGaP and AlInP.\(^{66,67}\) If ordering is present, the observed shift corresponds to a change in the InGaP order parameter from \(\eta\sim0.33\) to 0.19. Less is reported on AlInP, and the effect that changing the order parameter has on the X-valley is unclear. An ordering-associated band-gap lowering effect that effectively changes AlInP from an indirect to a direct semiconductor has been reported in OMVPE-
grown AlInP; however, it is unlikely that MBE grown samples, with a corresponding low growth temperature, can display enough ordering to lower the direct band-gap the \( \sim 200 \) meV required for this effect.\(^{62}\) There are, however, some indications that ordering may play a role in the energy blue shifts noted here. Firstly, the observed 10 K InGaP NBE emission is approximately 50 meV lower than that expected for fully disordered material (i.e., 1.955 versus 2.005 eV), and the observed blue shift is consistent with anneal-induced disordering. Additionally, the blue shifted features are not interface-localized, demonstrated in Figure 4.24. While the lack of a spatial dependence to the InGaP emission energy is interesting, it is not definitively indicative of ordering since any interface disorder resulting from atomic cross-diffusion likely causes carriers to recombine preferentially towards the interfaces.
Figure 4.24: InGaP NBE emission energy versus interface position for all structures. No spatial dependence to the emission energy is noted.

The increase in the 1.8-2.1 \( V_P \) or Al-O emission relative to AlInP (Figure 4.13) with increasing anneal temperature is consistent with either the out-diffusion of P from AlInP or the in-diffusion of O from the SiO\(_x\) capping layer at high temperatures. Cs\(^+\) SIMS in Figure 4.4 shows an O distribution that is largest near the SiO\(_x\)-on-AlInP interface and decreases into the epilayers. This isn’t however, consistent with the XCLS line-profile results of Figure 4.9, which show that the 1.8-2.1 eV feature is not localized at the SiO\(_x\)-on-AlInP interface. Additionally, if the ratio of the SIMS-measured O to P is calculated in the regions of interest (i.e., the inner and outer AlInP layers), shown in Figure 4.25, it is demonstrated that this ratio only changes significantly for both layers at...
850°C. This is not consistent with Figure 4.13, which demonstrates that the deep level emission increases relative to AlInP after annealing at temperatures as low as 650°C. This indicates that $V_P$ is the more likely cause of this emission. That these increases begin to occur relatively close to $T_{\text{growth}}$ is significant for devices, where $V_P$ can degrade performance by introducing new recombination pathways.

![Figure 4.25: Ratio of SIMS-measured O to P taken in the middle of the inner and outer AlInP epilayers. The ratio does not increase for the innermost AlInP layer until annealing at 850°C. This demonstrates that the observed increase in ~1.8-2.1 eV emission intensity with annealing (which starts at 650°C) is due to $V_P$ formation rather than O incorporation in the AlInP layers.](image)

The 1.49 eV feature observed in the IR-XCLS spectra increases after annealing at 750 and 800°C. This could be due to the in-diffusion of Si into GaAs from the outermost (SiO$_x$ and buffer/substrate) layers. This scenario is consistent with Figure 4.21, which shows that the relative 1.49 eV intensity is maximized towards the interfaces. While
SIMS shows no significant Si diffusion from the SiO$_x$ cap into the innermost InGaP layers, some trace amount from the substrate might occur and can explain this result.

The ~1.25-1.45 eV broad, GaAs-on-InGaP localized feature is consistent with the formation of an InGaAs-like interfacial layer. Since the band-gap of this layer is smaller than that of either GaAs or InGaP, carrier confinement will be particularly strong and optical emission intensity is expected to be high, as observed. A 5-20\% In incorporation into the GaAs layer results in emission energies in the range reported here and is consistent with the XSTM results of Feenstra et al., the observation of In segregation on InGaP surfaces, and its subsequent incorporation into GaAs layers.$^{45,68,73,74}$ Furthermore, the asymmetric interface behavior of this emission is consistent with the thicker GaAs-on-InGaP interfacial layer relative to InGaP-on-GaAs that is reported.$^{68}$ Alternatively, an As-P exchange reaction, or diffusion resulting from the As soak on InGaP, could result in an InGaAs-like layer. Inhomogeneities in the interfacial layer may explain the number of different features observed in Figure 4.18. As interfacial cross-diffusion begins during annealing such a layer is expected to smear. Cross-diffusion that results in a thinning of the interfacial layer is consistent with a blue shift of the optical emission. For higher temperatures, where the cross-diffusion of atoms is large relative to the interfacial layer width, a homogenization of the InGaAs-like layer with the cladding layers could quench the emission. This is consistent with the behavior observed at T $\geq$ 750$^\circ$C in Figure 4.18, and with the SIMS profiles of Figure 4.14 and Figure 4.15. While a “deep emission” peak has been reported at this (ordered) interface, it is unlikely to be the same emission reported here as the feature is typically not seen unless the InGaP NBE emission is $< 1.9$ eV, indicating a strongly ordered InGaP layer.$^{45-48}$ The presence of $V_{As}$ acceptor
complexes having a similar energy is a possibility but is unlikely since similar features are not observed in the AlInP/GaAs DH with identical GaAs growth conditions.\textsuperscript{150}
4.6 Results for Metamorphic Junctions

It is of considerable interest to the research and device communities to expand on the current platform of devices by growing new compositions on conventional substrates. To sidestep the requirement of lattice-matched overlayers, growers are experimenting with the use of graded buffer layers. In such a graded buffer layer the grower builds up to the desired composition by growing successively more mismatched layers. To compare a junction of this type to the previously studied systems, a metamorphic \( \text{In}_{0.63}\text{Ga}_{0.37}\text{P}/\text{In}_{0.15}\text{Ga}_{0.85}\text{As} \) DH grown on a graded buffer layer is examined. This structure is shown pictorially in Figure 4.26. Growth parameters are similar to those used in the previous structures. \( \text{Cs}^+ \) and \( \text{O}_2^+ \) SIMS profiles are shown in Figure 4.27, clearly demonstrating the graded nature of the structure.

Figure 4.26: Picture of a metamorphic InGaP/GaAs DH grown on a step-graded buffer layer.
Figure 4.27: Cs\(^+\) (top) and O\(_2^+\) (bottom) SIMS profiles for an In\(_{0.15}\)Ga\(_{0.85}\)As/In\(_{0.63}\)Ga\(_{0.37}\)P DH grown on graded InGaAs/GaAs. The graded nature of the buffer layer is clearly visible from the O\(_2^+\) SIMS profile.

XCLS spectra are shown in Figure 4.28. The spectra exhibit 1.75-1.85 eV In\(_{0.63}\)Ga\(_{0.37}\)P NBE and DA features, as well as a broad GaAs substrate emission. The InGaAs graded buffer layers have E\(_g\) < 1.40 eV and are not visible in Figure 4.28.
None of the lower energy, 1.25-1.45 eV emission observed in the lattice-matched InGaP/GaAs DH is apparent in Figure 4.28. Figure 4.29 shows an analysis of the features observed in Figure 4.28 including integrated In\textsubscript{0.63}Ga\textsubscript{0.37}P intensity, In\textsubscript{0.63}Ga\textsubscript{0.37}P emission energy, and In\textsubscript{0.63}Ga\textsubscript{0.37}P FWHM, along with an analysis of the non annealed InGaP/GaAs DH for comparison purposes. The intensity behaves as expected, being maximized in the InGaP layers; however, it is ~10X lower in the InGaP/GaAs DH grown on a graded buffer layer, indicating a lower radiative emission efficiency possibly due to a higher dislocation density. Emission energy is lower due to 63% In versus 51% in the lattice-matched structure. It is noted that the In\textsubscript{0.63}Ga\textsubscript{0.37}P NBE emission is ~10 meV lower in the outer In\textsubscript{0.63}Ga\textsubscript{0.37}P layer versus the inner In\textsubscript{0.63}Ga\textsubscript{0.37}P layer, possibly due to a small change (~1%) in In/Ga ratio for the two layers. FWHM, which is inversely related
to layer quality, is ~2X higher in the $\text{In}_{0.63}\text{Ga}_{0.37}\text{P}$ layers grown on a graded buffer layer relative to InGaP grown on GaAs. Thus, XCLS can be used as a sensitive probe of epilayer quality in these structures.

![Graph showing CLS features of InGaP layers](image)

Figure 4.29: Analysis of InGaP CLS features observed in Figure 4.28. The InGaP layers grown on a graded buffer layer are compared to those from Figure 4.17.
4.7 Conclusions

Depth-resolved SIMS is used to show that controlled anneals of SiO$_x$ capped InGaP/GaAs and AlInP/GaAs DHs produce > 100 nm interfacial diffusion on the Group-III and Group-V sublattices. In both cases, structures are abrupt with annealing at $T \leq 750^\circ\text{C}$, and diffusion occurs rapidly for $T \geq 800^\circ\text{C}$. Diffusion due to IILD resulting from the in-diffusion of Si from the capping layers and substrate is unlikely to occur, though out-diffusion of metal atoms from the epilayers is observed and could result in a formation of vacancies that facilitates the diffusion observed at high temperatures. Additionally, a two-stage Fickian process with activation energies of $\sim 7.5-11$ and $\sim 0.5-1.5$ eV has been measured for the cross-diffusion of As and P at AlInP/GaAs heterointerfaces.

Cross-sectional CLS reveals 20 and 40 meV blue shifts of InGaP NBE and AlInP X-band emission in these structures after 850$^\circ\text{C}$ anneals. These shifts can be explained by the in-diffusion of Ga from the GaAs epitaxial layer, though partial ordering can not be ruled out. A broad, $\sim 1.8-2.1$ eV feature has been identified and spatially localized to within the AlInP film. This feature increases in intensity relative to AlInP emission at anneal temperatures as low as 650$^\circ\text{C}$, and is consistent with an increase in $V_P$. Despite the strong Al-O bond, this defect has been ruled out by a SIMS analysis that demonstrates no increase in O incorporation in the AlInP layers until significantly higher temperature anneals. XCLS identifies a $\sim 1.25-1.45$ eV deep emission spatially-localized at the GaAs-on-InGaP interface. The spectral weight of this feature increases in energy and decreases in intensity after the highest temperature anneals where significant SIMS diffusion is identified. This is consistent with a thin InGaAs-like interfacial layer reported to form at
this interface. Changes in the dimensions of this interfacial layer and a homogenization of interface composition resulting from annealing explains the $T \geq 750^\circ$C behavior of the emission. An increase in a 1.49 eV DA-related feature could be due to some incorporation of Si near the InGaP/GaAs interfaces. Overall, these results demonstrate the potential of XCLS as a sensitive probe of interface and bulk electronic structure, and further correlate this structure with cross-diffusion and exchange reactions similar to those that may occur during device operation or the early stages of interface growth.
5.1 Summary of Results

Overall, the goal of this thesis is to explore the physical and electronic structure of a number of III-V lattice-matched heterojunctions known to be susceptible to interfacial cross-diffusion and exchange reactions. The effects of diffusion resulting from varying growth parameters, as well as post-growth annealing, are quantified. It is demonstrated that bulk and interface-related defect states depend sensitively on the nature of these growths and anneals. The results of these measurements clarify the interface formation process, interface behavior with annealing, and the nature of bulk and interface electronic states in III-V compounds with similar growth transitions.

In chapter three, interfaces in InGaAs/InP DHs are studied. SIMS is used to demonstrate ~8 nm interfacial broadening as a result of increasing the As soak time at the InGaAs-on-InP interface from 20 to 150s. This broadening is due to As incorporation into the InP lattice, and shows no saturation effect for soak times up to 150s (i.e., the interface width continues to increase). Ga-P bonding is identified at both the InGaAs-on-InP and InP-on-InGaAs interface. This Ga-P bonding counter-intuitively increases with an increasing As soak at the InGaAs-on-InP interface. In structures exposed to the longest As soak, which therefore demonstrate the most Ga-P bonding, the Ga-P profile is
observed at a shallower depth relative to As than the Ga-P profiles for structures with a shorter As soak. The position of and increase in Ga-P bonding is attributed to an enhancement of P diffusion owing to the mixed-anion InAsP lattice that results from an extended As soak. The InP-on-InGaAs interface exhibits no significant broadening as a function of P soak time. Thus, while a thin InGaAsP interfacial layer is reported to form at this interface, no additional interfacial broadening is observed with P soak times from 60-150s. This is consistent with an interfacial layer that forms quickly due to the high thermodynamic stability of Ga-P versus In-P. After this layer formation, no further interfacial diffusion or Ga-P bonding occurs.

These results have clarified the nature of the competition of atomic species in the interface region during growth, and highlight the asymmetric behavior of the interfaces. Figure 5.1 demonstrates this picture of InGaAs-on-InP interface formation.

Figure 5.1: Pictorial demonstration of the effect of an extended As soak on the just-grown InP surface. Longer As soaks lead to more As incorporation as P desorbs and leaves vacancies.
To elaborate, it is known that As quickly replaces P to form a highly strained InAsP layer during an As soak on InP.\textsuperscript{5-10} Due to the elevated growth temperature, Group-V atoms will desorb from the just-grown surface; however, As atoms can be replaced by vaporous As present during an As soak. This is in contrast to P, which is rapidly evacuated from the growth chamber after the source is closed, and is therefore unable to supply the semiconductor with enough P to replace desorbing P atoms. These desorbing P atoms leave behind vacancies. Readily available As diffuses into the InP layer via a Frank-Turnbull mechanism to form a thicker InAsP layer than the few monolayers over which As-P exchange is reported to occur.\textsuperscript{10} While this layer is highly strained, no relaxation is anticipated for thicknesses less than $h_c$. The width of this InAsP transition region is largely dependent on $T_{\text{growth}}$ and such variables as the As and P beam pressures, but is measured to be a total of $\sim 8$ nm in the most diffused structure studied here.

After the As soak on the InGaAs-on-InP interface, the In and Ga sources are opened and InGaAs growth begins. Owing to its stronger bond, Ga competes favorably with In to bond with any accessible P, leading to some Ga-P bonding in the InGaAs-on-InP interface region, even for abrupt structures with a short interface As soak time. For longer As soak times, less P is accessible in the near-surface region; however, an increase in Ga-P bonding is observed in these structures in Figure 3.7. Therefore, it is likely that the highly disordered InAsP layer the forms from an extended As soak, full of charged point-defects that enhance diffusion, as well as some mobile P that didn’t desorb from the surface, encourages the out-diffusion of P. This mobile P then bonds with Ga atoms in the growing InGaAs layer. Consistent with Figure 3.6, this leads to a shallower
InGaAs-on-InP interface Ga-P bonding profile relative to As in the structures with the longest As soak time. Figure 5.2 demonstrates the formation of interfacial Ga-P bonds.

At the InP-on-InGaAs interface, no change in interface width is observed for P soak times from 60-150s. Since it is reported that an InGaAsP layer forms at this interface, these results suggest that this thin interfacial layer forms quickly and, under the growth parameters used here, does not increase in width with further P soaking. This is supported by Figure 3.32, which demonstrates that Ga-P bonding does not change in intensity with P soak time at the InP-on-InGaAs interface. For P diffusing into InGaAs, the Ga-P signal is expected to increase in intensity.
These dramatic differences in interface behavior are expected to manifest themselves electronically. CLS shows some evidence for compositional rearrangement at the InP-on-InGaAs interface. Dual peaks are observed in both the structure exposed to the longest P soak time at the InP-on-InGaAs interface, and in several of the structures exposed to a long As soak time at the InGaAs-on-InP interface while the InP-on-InGaAs interface P soak time is held constant. Since the SIMS profiles at the InP-on-InGaAs interface are constant for all structures, CLS may be reflecting small differences in this interface not detected by SIMS. A low energy feature observed closer to the InP-on-InGaAs interface in structures exposed to the longest As soak times at the InGaAs-on-InP interface may demonstrate this behavior due to a lower radiative recombination efficiency at the InGaAs-on-InP interface. In addition to these CLS observations, a novel technique has been used to accurately measure the InGaAs/InP $\Delta E_c$, and to demonstrate the possibility of a decrease in $\Delta E_c$ with a longer As soak time. After the analysis of growth-diffused structures, annealing in UHV at temperatures from 440-495°C is used to demonstrate interfacial diffusion of ~60 nm. This diffusion is modeled by a Fickian process with $E_{\text{act}}^{\text{As-P}} = 2.29 \pm 0.13$ eV and $D_0^{\text{As-P}} = 1.45 \text{ cm}^2/\text{s}$.

It is desirable to generalize these results to III-V systems with similar growth transitions. InGaP/GaAs and AlInP/GaAs interfaces are similarly susceptible to As-P exchange reactions and have similar Group-III concentration gradients. Results obtained from annealing these structures are the subject of chapter four. Significant interfacial diffusion in SiO$_x$-capped structures is demonstrated after 1 hour anneals at temperatures $\geq 800^\circ$C. The activation energy of a two-stage Fickian diffusion process in AlInP/GaAs has been measured with $E_{\text{act}}^{\text{As-P}} \sim 7.5-11$ eV and $\sim 0.5-1.5$ eV respectively.
Using XCLS, defect emissions in both InGaP/GaAs and AlInP/GaAs DHs are identified. A 1.8-2.1 eV emission is observed in AlInP/GaAs. This defect is localized to the AlInP layer and increases after annealing at temperatures close to the 490-565°C $T_{\text{growth}}$. This increase is attributed to the anneal-induced formation of $V_P$. In InGaP/GaAs, a broad ~1.25-1.45 eV emission is spatially localized to the GaAs-on-InGaP interface using CLS line scans and imaging. Annealing shifts the spectral weight of this emission to higher energies and decreases its intensity. This is consistent with the cross-diffusion and homogenization of an InGaAs-like interfacial layer thought to form at this interface.\textsuperscript{68}

The strength of the Al-P bond precludes a large amount of Al diffusion. Since In-P and Ga-As bonds are weaker than Al-P, Ga and In are expected to preferentially diffuse across the interface. This diffusion is marked by the further incorporation of Ga into the InGaP/AlInP ternary layers, and by In from these ternaries diffusing into GaAs. The incorporation of Ga at the expense of In in the ternaries explains the 20 and 40 meV shifts in the InGaP NBE and AlInP X-band emissions observed by CLS and shown in Figure 4.11 and Figure 4.23. This picture of diffusion and interface behavior is demonstrated in Figure 5.3.
An InGaAs-like interfacial layer is identified at the GaAs-on-InGaP interface. Cross-diffusion during annealing, demonstrated for both InGaP/GaAs and AlInP/GaAs DHs, not only smears the InGaAs-like layer, reducing its intensity, but also blue shifts the CLS emission in InGaP and AlInP layers.

Figure 5.3: An InGaAs-like interfacial layer is identified at the GaAs-on-InGaP interface. Cross-diffusion during annealing, demonstrated for both InGaP/GaAs and AlInP/GaAs DHs, not only smears the InGaAs-like layer, reducing its intensity, but also blue shifts the CLS emission in InGaP and AlInP layers.

It is reported that the InGaAs-like interfacial layer that forms at the InGaP-on-GaAs interface is thinner than the 3-4 bilayers that form at the GaAs-on-InGaP interface. This bears a striking resemblance to the behavior observed in the InGaAs/InP structures studied in chapter three. During growth at the GaAs-on-InGaP interface, the slow diffusion of As into InGaP at the expense of P may result in an InGaAs-like layer and the observed 1.25-1.45 eV emission. This is consistent with the As replacement of P during an As soak at the InGaAs-on-InP interface. That the 1.25-1.45 eV emission is not observed at the InGaP-on-GaAs interface is consistent with the result obtained via an extended P soak at the InP-on-InGaAs interface (i.e., that an increasing P soak does not result in a broadened interface). This result can be extrapolated to suggest that P does not necessarily replace As during a P soak at the InGaP-on-GaAs interface. Thus, when P is soaked on the GaAs interface for 20s prior to InGaP-on-GaAs interface growth, little
replacement occurs and only a minimal if any InGaAs-like layer forms. Therefore, the asymmetric interface behavior identified by SIMS in the InGaAs/InP system also occurs in the InGaP/GaAs system, where it manifests itself as an InGaAs-like interfacial layer identified and spatially localized by CLS to the GaAs-on-InGaP interface.

5.2 Future Work

This project, being ambitious in its goal of making generalizations regarding III-V heterointerfaces, has a number of natural extensions for the interested researcher. Proposed experiments include:

(1) The SET technique needs to be further refined and extended to additional material systems including InGaP/GaAs and AlInP/GaAs, the latter being particularly difficult due to the tendency of Al to oxidize. Contamination resulting from higher-than-ideal pressures in the process/cleaving chamber has been an issue and, since this can pin $E_F$, it potentially skews measurements. While the chamber is capable of pressures in the $5 \times 10^{-10}$ torr range, these are not maintained for long times after baking. Furthermore, frequent intro-chamber venting due to the difficulty of achieving a good cleave can compound this. A new cleaving apparatus would be helpful, as would experiments designed to explore different pumping strategies during cleaving. The effects of primary beam conditions on SET measurements are also important and are not fully understood at this time.

(2) A detailed description of the ordering process and the behavior of long-range ordered overlayers is beyond the scope of this thesis. The possibility of some
ordering in the ternary constituents of the InGaP/GaAs and AlInP/GaAs DHs analyzed here should be explored. X-ray diffraction (XRD) measurements may be able to clarify this. Some data on the effects that LRO has on the X-band may be necessary to examine the observed optical changes in the AlInP/GaAs DH.

(3) TEM or XSTM measurements designed to provide direct confirmation of the interfacial layers posited here for InGaAs/InP, InGaP/GaAs, and AlInP/GaAs, would be useful. These techniques may provide information on the width and composition of these layers.

(4) An interested theorist might be able to further explain some of the more interesting results in this thesis. It is interesting that As seems to replace P, but P does not seem to replace As in the systems studied. Though there is some disagreement on this in the literature, the stronger P bonding seems to suggest that the opposite behavior is more likely. This paradox may be a function of the growth conditions used, and the number of in-grown versus thermally created vacancies. Calculations of the expected behavior with annealing of the InGaAs-like interfacial layer posited to form at the GaAs-on-InGaP interface would be useful. Diffusion is proposed to explain the shift to higher energies of the spectral weight of the 1.25-1.45 eV emission; however, it is not clear whether or not this is consistent with the quantitative measurements of other authors. It is known that In-Ga cross-diffusion is significantly greater than As-P. The effect of this diffusion on the layer dimensions and corresponding optical emission would be helpful in resolving the nature of the changes observed here with annealing. Additionally, calculations of the expected $\Delta E_c$ at the InGaAs-on-InP
heterointerface as a function of InAs\textsubscript{x}P\textsubscript{1-x} interlayer composition (i.e., strain) and defect formation would be useful in explaining the nature of the chemical interlayers and defects that form at this interface and influence its electronic properties.

(5) It would be interesting to extend the work on As and P soak time to the InGaP/GaAs and AlInP/GaAs interfaces. In these systems As is the binary anion which contrasts with As as the ternary anion in InGaAs/InP. Also, the strongest bonds in the InGaP/GaAs and AlInP/GaAs systems are in the ternary rather than binary semiconductors. A different diffusion dynamic may be expected due to these differences in bonding. This study might help to clarify the role that bulk thermodynamics have on interfacial reactions.

(6) The effect of an extended interface soak time on carrier transport across the interface is an interesting extension of the work reported in chapter three. This could be performed with XCLS as the beam is positioned at points approaching the interface and the intensity monitored. Some modeling of carrier diffusion dynamics would be necessary.

(7) The work of chapter three demonstrates the potential for some control over $\Delta E_c$ at InGaAs/InP junctions. Since $\Delta E_c$ places boundary conditions directly on the Schrödinger equation, such control has important implications for electronic devices. Growths where the interface As soak time at InGaAs/InP quantum well junctions is systematically varied could demonstrate the ability to tailor optical emissions and confinement characteristics. These devices can be studied by
optical methods including CLS, and raise the possibility of a commercially-relevant application of the fundamental results demonstrated in this thesis.
LIST OF REFERENCES


115 H. Lüth, Surfaces and Interfaces of Solid Materials, (Springer-Verlag Berlin Heidelberg, (1997)).


120 P. Hovington, D. Drouin, and R. Gauvin, Scanning 19, 1 (1997).


122 D. R. Vij, Luminescence of Solids (Plenum, New York, New York (1998)).


http://www.cea.com/cai/simstheo/beameff.htm


http://www.veeco.com/library/resources.php


