Dry Passivation Studies of GaAs(110) Surfaces by Gallium Oxide Thin Films Deposited by Electron Cyclotron Resonance Plasma Reactive Molecular Beam Epitaxy for Optoelectronic Device Applications

by

Danny Kim

A thesis submitted in conformity with the requirements for the degree of

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in the

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Abstract

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Master of Applied Science in Materials Science Engineering

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Professor Harry E. Ruda, Thesis Supervisor

This study introduces a novel method for surface passivation that addresses the inherent problems of GaAs-based optoelectronic devices. Performance and reliability of these devices, when insufficiently passivated, are often limited by excessive non-radiative recombination due to a high density of surface states in the forbidden gap. These surface states originate from the accumulation of elemental Arsenic and As_{Ga} antisites in the near-surface region, owing to decomposition of Arsenic Oxides, and/or from increased surface disorder. This problem is addressed by depositing a nanometer-thick layer of Gallium Oxide on clean GaAs, and improves upon existing technology by using high purity sources in an ECR-MBE deposition process, signifi-
cantly reducing contamination and surface damage, respectively. Room temperature photoluminescence spectra show an enhancement in luminescence efficiency by greater than an order of magnitude, which is corroborated by low temperature spectra that show reductions in specific mid gap recombination channels. This enhancement is the result of reduced surface state density made possible by the hydrogen passivation of EL2 defects, and from the smooth, stoichiometric, thermodynamically stable Gallium Oxide thin film overlayer that prevents Arsenic Oxide formation.
"Yet we should not minimize our sacred endeavours in the world, like faint glimmers in the dark, we have emerged for a moment from the nothingness of unconsciousness into material existence. We must make good the demands of reason and create a life worthy of ourselves and of the goals we only dimly perceive."

Andrei Dmitrievich Sakharov (1921-1989)
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"For God's sake, Edwards.
Put the laser pointer away."

Courtesy of the New Yorker Magazine
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Part I

Introduction and Theory
Chapter 1

GaAs in 2001

1.1 GaAs: Let there be quantum-efficient light

The importance of GaAs-based optoelectronic devices cannot be overstated. Ubiquitous revolutionary technologies such as the internet, CD-ROM and DVD are in part attributable to the solid-state semiconductor diode laser; this has literally and figuratively, been a quantum leap for science. These devices— which include edge-emitting laser diodes (EELD), light emitting diodes (LED), and vertical cavity surface emitting lasers (VCSEL)— offer tremendous advantages over previous methods of light generation. They are more compact (devices at most are a few microns cubed), generate more photons per injected carrier, and possess spectral output characteristics affording a range of new applications, as well as enhancing performance in existing applications. By alloying GaAs with Indium, Aluminum, or Phosphorus (or any per-
1.1. GaAs: Let there be quantum-efficient light

mutation of these elements), the emission wavelength can tuned to span from visible to near-infrared wavelengths. In the visible range, GaAs has supplanted inferior light emitting technologies: bulky HeNe lasers for bar code scanning have been replaced with compact, low-power consumption AlGaAsP lasers; incandescent bulbs for traffic lights are replaced with longer lifetime, higher brightness LED’s. Slightly above the visible threshold, GaAs-based EELD’s have revolutionized data storage and retrieval by supplanting analogue, sequential magnetic tape with highly reliable, high-density storage media of CD-ROM and DVD. Having higher data density allows for quicker data retrieval, thus enabling high quality video playback. Other applications that are particularly suitable for GaAs-based lasers include laser hair removal, whitening of the teeth, arthroscopic surgery, and materials cutting or marking. The scope of application is continually being investigated for medical purposes. GaAs-based EELD’s are also used to pump solid state lasers, which they do with greater quantum efficiency than flash-lamps. The most lucrative application by far, is in fibre optic communication systems.

GaAs-based lasers are major components in such fibre optic networks. Optical signals are transmitted in the 1500 nm wavelength range, to take advantage of the attenuation minima of optical cable. GaAs-based vertical cavity surface emitting lasers (VCSEL) emit in this range and can currently modulate signals at a rate of 2.5 Gbps and soon, 10 Gbps. These signals can travel a few hundred kilometers before they are attenuated below detection limits. Devices known as Erbium Doped
Fiber Amplifiers (EDFA) utilize InGaAs lasers emitting at 980 nm to reamplify signals. This technology is especially favorable since it introduces little noise, and in a Wavelength Division Multiplexed (WDM) signal where 16 or more different colors are transmitting data, EDFA's can amplify all the signals simultaneously.

For most of the aforementioned applications, higher maximum output power is desired. Higher power can benefit the applications in the following ways: for optical storage faster rewrite speeds can be obtained; for materials processing, thicker cuts in shorter time can be made; higher power solid state lasers can be attained with higher power laser diode-pumps. The most important application where higher power is required, is of course, fibre optics. Higher power EDFA pump lasers are key in attaining a lower cost network. By increasing the output power of the pump lasers, the signal can travel further before regeneration is needed again. This is especially important in trans-oceanic network deployment where the cost of installing EDFA's can amount to the majority expense of the network. Also, the more EDFA's that are installed, the greater chance there is that one of them may fail. If they do fail, a service call can cost in the order of a million dollars.

The need for reliable and powerful amplification can only increase with the inevitable industry-wide transition to an all-optical network. This technology will not have optical-electrical-optical (OEO) conversion to regenerate the signal, therefore will be faster, and cheaper, but introduces loss since the components inside these switches consist of mirrors and lenses. This loss must be compensated for by ampli-
1.2 Laser Diodes: Catastrophic Failure

At low power operation, GaAs edge emitting laser diodes are highly reliable. They can be operated in excess of 10^6 hours without loss of output power or change in operating characteristics. When operated at high powers, however, reliability is drastically reduced. If the optical power density at the output facet operates in the range of 6-12 MW/cm² or greater, the laser is in danger of failing catastrophically[22]. The failure originates from a large proportion of carriers recombining non-radiatively at the facet, producing an intense concentration of heat, enough to melt the semiconductor. This phenomena is known as Catastrophic Optical Damage or thermal runaway, since the laser fails suddenly by very rapid heating.

Catastrophic Optical Damage (COD), begins with a laser that has a high surface state density at the output facet. These surface states introduce channels for non-radiative recombination, which generate heat. This heat will shrink the band gap, increase oxidation of the facet, and create more defects, which in turn create more channels for non-radiative recombination, which creates further heat. This feedback loop will continue to generate heat, causing rapid failure by melting of the output facet (1500K). See Figures 1.1 and 1.2.

The COD loop, oxidation loop, and defect loop, are all interrelated, and all lead to non-radiative recombination. To prevent the catastrophe, each of these loops must
1.2. Laser Diodes: Catastrophic Failure

Figure 1.1: Flow diagram showing all the cumulative factors which contribute to catastrophic failure
1.2. Laser Diodes: Catastrophic Failure

Figure 1.2: SEM image of the front facet of a laser diode that underwent COD. Source: Mallard et al. 1998[1].

be eliminated. Further facet oxidation can be prevented by encapsulating the surface with a dielectric, but non-radiative recombination will still occur from the existing surface states. Defects can never be eliminated, but can be minimized with low energy processing, and further defect creation and growth can be prevented by reducing non-radiative recombination. To totally prevent COD, heating of the facet must be stopped, and this can be mitigated to a certain extent by heat-sink engineering, or laser-diode design, but a more effective method, and the aim of this thesis is to address the fundamental issue, the source of the heat: non-radiative recombination. Non-radiative recombination is caused by surface states in the forbidden gap. The goal then, is to identify these surface states, and determine their origin, in order to
be able to minimize them. This is done by what is known as “passivation”.

1.3 Surface Passivation: Criterion

Surface passivation of a semiconductor involves deposition of a thin film of another semiconductor or insulator on the surface to preserve or enhance the properties of the device. And, in order for a passivation layer to be beneficial, chemical, electrical, and mechanical requirements must be considered.

Chemical and electrical passivation is not mutually exclusive, and are of equal importance. Chemically, the passivation layer must saturate the dangling bonds to prevent alteration of surface chemistry; these bonds must be thermodynamically stable under atmospheric pressure and in the operational temperature range. With thickness in the nanometer range, it must prevent diffusion, both inward and outward, to protect and preserve. It should compensate the excess charge at the surface, or produce controllable band bending so as to drive carriers away from the surface. The main electrical requirement for passivation is that it must not introduce further states into the forbidden gap. Also, the band structure of the substrate and the overlayer should be that of a type I heterostructure, where the overlayer straddles the substrate, thereby confining the charge carriers to the bulk.

The last requirement for an effective passivation layer is structural. Upon deposition it must not damage the surface – the ion energies must be sufficiently low in order not to introduce bombardment-induced defects. After deposition, it is preferable that
the layer be lattice matched or amorphous in order not to create any strain-induced defects. For GaAs ($a_o=0.565$ nm), this limits the choice of lattice-matched crystalline passivation layers to ZnSe ($a_o=0.567$ nm, $E_g=2.70$ eV) and Ge ($a_o=0.567$ nm, $E_g=0.81$ eV). Note that this lattice match requirement is only important for thick crystalline coverages – for thin coverages (20-40 Å), the film itself will not impart but will be subject to biaxial strain.

As device size becomes smaller, the importance of surface passivation will become increasingly important, due to the increase in the surface to volume ratio.

1.4 Objective of this Thesis

The objective of this thesis is to investigate passivation methods using Electron Cyclotron Resonance plasma reactive Molecular Beam Epitaxial (ECR-MBE) deposition on surfaces of GaAs(110). The motivation for the selection of the GaAs(110) surface is that these surfaces form the Fabry-Pérot facets of semiconductor laser diodes. It is important to note that the majority of research has gone into passivation of GaAs(100) surfaces, which benefit electronic devices. Most studies have been empirical with the (110) plane; laser diodes were manufactured, and passivated with a process, but detailed data that corroborates the improvements is sparse. (100) and (110) surfaces differ in structure, reactivity[2] and passivation receptiveness[23]; further investigation into the GaAs(110)-insulator interface is required.

The bulk of this study focuses on passivation by Ga$_2$O$_3$ deposited by ECR-plasma
1.4. Objective of this Thesis

The oxidation of gallium evaporated by a Knudsen cell. To my knowledge, this has never been attempted before. The reason for the choice of this process for passivation is founded on material, electrical, and optical requirements. It has already been demonstrated that Ga$_2$O$_3$ is exceptionally beneficial for GaAs(100) surfaces, and InGaAs laser diodes[24]. However limitations of this process include impurity incorporation (Gd up to 1.5%), loss of stoichiometry without oxygen background pressure, unavailability of single crystal Ga$_2$O$_3$ – only powder packed forms are available. Ga$_2$O$_3$ has also been deposited by rf-plasma oxidation of gallium evaporated by e-beam[25], but unsubstantial results can be explained from their selection of the sources: gallium is not traditionally evaporated from an e-beam source; but more significantly, rf-plasma can induce surface damage since ion energies are in the order of keV. ECR-plasma has ion energies in the range of 10-30 eV, which eliminate the possibility of bombardment-induced surface damage. Native oxides and organic contaminants can be selectively removed at room temperature by hydrogen ECR plasma[26], whereas thermal desorption requires extreme temperatures and does not remove as much carbon[27].

Another advantage of the ECR-MBE process is that it is more versatile; with the introduction of a gas manifold near the substrate, other dielectrics such as Si$_3$N$_4$ and SiO$_2$ can be deposited.

The question has not been answered then whether an improvement of the aforementioned can be attained by using high purity sources in a low energy deposition process. Besides these advantages, does the fact that the deposition is a CVD
1.4. Objective of this Thesis

process as opposed to PVD with the e-beam evaporation process effect passivation effectiveness? Can smooth stoichiometric films be formed? How do these films interact electronically with the substrate? How does the hydrogen ECR cleaning affect properties of the semiconductor?
Chapter 2

GaAs Physics

2.1 III-V Semiconductor Surfaces

2.1.1 III-V Semiconductors

The crystal structure of most III-V semiconductors is the zinc blende, or sphalerite structure. This structure can be described as two interpenetrating Face Centred Cubic (FCC) unit cells, offset by $\frac{1}{4}(111)$, where the group III and V atoms reside on different sublattices. Atoms form $sp^3$ hybrid orbitals, with each atom tetrahedrally coördinated by its four nearest neighbors. In the bulk, each group III(V) atom is bonded to four group V(III) atoms. The bonds are partially-ionic, owing to the higher electronegativity of group V atoms. The ionicity of these bonds will favor cleaving on the charge-balanced (110) plane rather than the (111) plane, even though a greater number of bonds is required to be broken. In the case of non-polar bonding
2.1. III-V Semiconductor Surfaces

2.1.2 GaAs(111): Cation or Anion

Ideal (111) planes terminate in either only Ga atoms or only As atoms. This can occur by severing the bonds along an AB type plane (see Figure 2.2). Severing along AB is preferred as only one bond needs to be broken for each Ga and As pair, while severing along the AB plane requires three bonds per atom to be broken, and is thus energetically unfavorable. The Ga-terminated (111) surface tends to be less reactive than the As-terminated (111) surface since the As atoms have nearly-filled dangling bonds.
Figure 2.2: Ideal GaAs crystal structure, showing (111) surfaces terminated by anion or cation. Source: Gatos 1994[2]
2.1.3 GaAs(100): Inherent Complexity

The GaAs(100) surface has been the most studied surface, principally, owing to its technological importance for fabricating semiconductor devices. The great majority of electronic and optical devices are grown on (100) substrates, and most passivation research has focused on (100) surfaces, in order to improve device performance. Epitaxial layers grown by MBE tend to grow smoothly on such surfaces, since the ideal (100) plane consists of only Ga or As atoms. As$_2$ flux will have a sticking coefficient of nearly 1 with Ga terminated surfaces, and nearly 0 with As-termination[3].

Another reason the (100) surface is selected for semiconductor growth, especially for laser diodes, is that the cleavage planes will form a Fabry-Pérot cavity. Using a (110) wafer would have the facets at a 45° angle to the growth surface, since the cleavage plane for a (110) oriented wafer is the (101) plane.

(100) surface atomic organization tends to be highly complex, undergoing reconstruction dependent on the temperature and stoichiometry. Ideally, the surface can consist of all cations or anions, but in GaAs, the As volatility will favor partial coverages, leading to various reconstructions. The mechanism behind surface reconstruction is to minimize the surface energy by minimizing the number of dangling bonds. On an ideal (100) surface each atom will have two dangling bonds and by forming dimers decreases the number of dangling bonds by two. Partial anion coverages creates surface meshes that are periodic on the surface. The unit mesh is denoted by vector notation where the two basis vectors point in the directions of $[\bar{1}10]$ and $[\bar{1}10]$. 
Figure 2.3: (Top Left) Side view of an idealized GaAs(100) surface. (Right) dimers at the surface are formed to minimize energy. (Bottom) Plan and side views of a (2x4) reconstruction. Source: Mönch 2001 pp.151,155[3].

The repeat unit is given in units of the bulk lattice vectors. For example, an As-rich surface will arrange itself in a c(4×4) structure (i.e. having a unit cell 4× larger in both dimensions than the bulk unit cell, and where ‘c’ denotes centered symmetry), and with decreasing As coverage, will form c(2×8), c(8×2) structures and further As desorption leads to Ga-rich 1×6 or 4×6 coverages.
2.2. Origin of Surface States

2.1.4 GaAs(110): Electrically Neutral

The surface of interest in this thesis is the (110) plane. When fabricating a laser diode the wafer is cleaved into rectangular bars, where the front and back (110) surfaces form a Fabry-Pérot cavity. The (110) surface is the preferential cleavage plane, since these surfaces are non-polar, and only weak van der Waals forces need to be overcome. The unit cell is electrically neutral, consisting of one cation and one anion. These atoms are in a zigzag arrangement of alternating cations and anions.

2.2 Origin of Surface States

2.2.1 Intrinsic Surface States

Surfaces result from the termination of the bulk, with the surface forming the interface between the bulk and vacuum. The surface atoms do not have the same periodic arrangement as bulk atoms, and this change from periodicity to vacuum will induce a change in properties. Typically, surface atoms have lower coordination numbers compared with bulk atoms, and more importantly, owing to the aperiodicity compared to bulk atoms, result in the formation of so-called surface states. Bands can form from these surface states and their occupancy establishes the net charge residing in the vicinity of the surface. Typically for so-called depleted surfaces, states which are closer to the conduction band are unoccupied and thus termed acceptor-like states, while those closer to the valence band are occupied principally and termed donor-like
Figure 2.4: Wavefunction of a surface state with tails into the vacuum and into the semiconductor. Source: Mönch 2001 p.35 [3].

states. For GaAs, the conduction and valence bands are principally derived from the Ga and As core states, respectively. Thus at the surface, Ga atoms contribute to acceptor like surface states, and As atoms contribute to donor-like surface states. Physically, the As atoms have nearly filled dangling bonds, while Ga atoms have nearly empty dangling bonds.

Using a one dimensional semi-infinite model, the wavefunction for an electron in a weak periodic potential is as follows [3]:

$$
\Psi_k(z) = A \exp(ikz) + B \exp[i(k - g_1)z]
$$

(2.1)

where $g_1$ is the unit vector of a reciprocal lattice, $k$ is the wavevector. In the bulk these Bloch waves exponentially grow as $z \to \infty$, and cannot be normalized, therefore cannot exist. However at the surface ($z \leq 0$), complex wavevectors are possible; electrons at the end of a one-dimensional chain have the complex wavevector:
2.2. Origin of Surface States

The wavefunction of these surface states decay into the vacuum exponentially, which manifest themselves as dangling bonds:

\[ k_{ss} = \frac{\pi}{a} + iq_{ss} \]  

(2.2)

\[ \Psi_{\text{vac}} = C \exp(px) \]  

(2.3)

where \( z < 0 \), and \( p \) is the decay parameter. For a more comprehensive analysis of intrinsic surface states by the nearly free electron model, or by the tight binding approximation, see Mönch 2001[3].

2.2.2 Intrinsic Surface States on GaAs(110)

Upon cleavage the GaAs(110) surface undergoes relaxation changing the surface band structure. This relaxation involves displacements of the surface atoms: the Ga atom is pulled in towards the bulk, and the As atom is pushed away from the bulk and simultaneously rotated. This relaxation behavior is the result of the combination of three physical mechanisms, which involve quantum-mechanical and classical electrostatic interactions. The first physical mechanism is due to the greater electronegativity of the anion. To minimize Coulomb repulsion energy between the valence band electrons of the anion and the surface atoms, the anion is pushed out of the bulk, as far as possible. This results in a change of bond lengths: the bond between the anion backbonded to the second layer cation will increase; the bond between
the surface cation and the surface anion will decrease, as will the bond between the surface cation and second layer anion, resulting in the cation being pulled in by the underlying anions and pushed into the bulk by the surface anion. The second relaxation mechanism deals with the hybridization behavior of the threefold-coordinated surface atoms. For GaAs, the Ga surface atom prefers $sp^2$ bonding (i.e. favoring planar geometry), but is constrained by underlying atoms. This explains the pulling of the Ga atom towards the bulk. Arsenic on the other hand prefers pyramidal $p^3$ bonding. The third physical mechanism deals with the location of the charge density maximum along the bond, i.e., ionicity. Ionicity determines the 'stiffness' of these bonds and the greater the ionicity, the less tilt of the surface anion. The surface cation is pulled in by the highly electronegative anions until it reaches its equilibrium position through Coulomb repulsion.

For GaAs(110) surfaces, anion-Coulomb repulsion, As-pyrimidal bonding, and Ga-planar bonding govern the relaxation behavior. The relatively small difference in electronegativity between Ga and As prevents significant bond length change; in fact \textit{ab initio} calculations of Sabisch \textit{et al.}\cite{4} show that bond lengths change length by 1\% (See Figure 2.5C bonds d1 and d3 shorten by 1\% and d2 lengthens by 1\%). In relaxed configuration the (110) surface consists of As atoms protruding out of, and Ga atoms pulled into the surface plane with a net displacement of 0.7 \AA, where the As bond is at a 30° angle to the ideal surface plane. By the third layer (Figure 2.5B), both Ga and As atoms occupy their ideal positions.
Figure 2.5: Ideal (left column) and relaxed surface of GaAs(110). Source: Sabisch et al. 1995[4].
The movement of the surface atoms will change the distribution of the localized surface states. The occupied As dangling bond states are shifted to a lower energy (i.e., below the valence band maximum), and the unoccupied Ga dangling bond states are shifted to higher energy (i.e., above the conduction band minimum). This results in the bulk bandgap being free of any intrinsic surface states. This has been observed experimentally for \textit{in situ} cleaved GaAs(110) surfaces, but not for MBE grown or Ion Bombardment and Annealing (IBA), where Fermi-level was found to be pinned at midgap, despite the Low Energy Electron Diffraction (LEED) spectra, indicating a well ordered surface[3]. The latter two preparation techniques produce surfaces with higher defect concentration, or surfaces with higher extrinsic surface state contribution, not observable by LEED.

\section*{2.3 Extrinsic Surface States}

For an ideal surface, intrinsic surface states arise from the reduced coordination of bulk atoms. This theory can be extended further, to explain surface states which arise from further deviation from ideal surfaces. Step edges on surfaces have more dangling bonds and create more surface states. Vacancies tend to create charge imbalance with respect to surrounding atoms, creating donor or acceptor-like states, depending on the missing atom site. This is also the case for antisite defects, where a cation(anion) is substituted for an anion(cation). Indeed, antisite defects are a major defects in GaAs.
2.3. Extrinsic Surface States

Chemisorption on ideal surfaces is also a source of extrinsic surface states. Adsorbates can alter the charge distribution near the surface; more electronegative atoms (e.g. chalcogenides and halides) tend to attract charge from the surface, while less electronegative atoms (e.g. alkali metals) tend to add charge to the surface. Physisorption is indeed detrimental, but more so for chemisorption: any adsorbent that modifies the original surface chemical structure will alter the intrinsic properties significantly. This is especially true for oxygen.

Significant progress in the understanding of the behavior of the electronic and structural characterization of surfaces, and species on surfaces came with the widespread use of atomic resolution scanning tunneling microscopy (See for example, [5]). The common misconception of point defects contributing highly localized discrete deep acceptors or donors at the point defect, was clarified using scanning tunneling spectroscopy (STS). STS spectra were used to measure interface state distributions as a function of position for MBE grown (100) surfaces, and revealed that the effective zone over which these defects were electrically involved was larger than anticipated (See Figure 2.6).

2.3.1 Native Oxide Formation on GaAs Surfaces

Adsorbates on semiconductor surfaces tend to perturb their intrinsic properties. Oxygen, adsorbed from the ambient, however is especially detrimental to GaAs surfaces. Fermi-level pinning on GaAs surfaces has been attributed to the native oxide
Figure 2.6: (a) STM image showing defects as bright colored spots. (b) Spatial distribution of interface states caused by point defects. Source: Hasegawa et al. 2000[5].
2.3. Extrinsic Surface States

<table>
<thead>
<tr>
<th>Mole Ratio</th>
<th>Oxide Composition</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pure</td>
<td>GaAsO₄</td>
</tr>
<tr>
<td>1:1</td>
<td>Ga₂O₃ + As₂O₃</td>
</tr>
<tr>
<td>1:2</td>
<td>Ga₂O₃ + As</td>
</tr>
<tr>
<td></td>
<td>GaAs</td>
</tr>
</tbody>
</table>

Table 2.1: Structure of oxidized GaAs surface as predicted from Ga-As-O ternary phase diagram. Source: Schwartz (1986)

formation, which cause an excess of anion formation in the surface region. The reaction of a GaAs surface with oxygen is energetically favorable, and a mixture of oxides form at the surface, including GaAsO₄, Ga₂O₃, As₂O₃, and As₂O₅[28]. The free energy of these species indicates that these oxide compounds are thermodynamically favored in an oxygen ambient over GaAs. The phases present in the native oxide are thus a function of depth, as predicted by the Ga-As-O ternary phase diagram (See Figure 2.7), with an expected oxide structure as shown in Table 2.1. However, it is the Arsenic oxide compounds that lead to the unfavorable surface properties due to its decomposition at the GaAs substrate forming elemental arsenic according to the reactions:

\[ 2GaAs + As₂O₃ \rightarrow Ga₂O₃ + 4As \quad \Delta G° = -259 \, kJ/mol \] (2.4)

The elemental As can then incorporate into Ga vacancies, forming the As₇Ga antisite defect, or between bonds as an interstitial Asᵢ. The accumulation of elemental As and the creation of As₇Ga antisite defects has been implicated in the mechanism for Fermi-level pinning for GaAs[6].
2.3. Extrinsic Surface States

2.3.2 Models for Extrinsic Surface State Formation

There is some controversy regarding the origin of extrinsic surface states on GaAs surfaces. It is commonly accepted that surface states originate from submonolayer coverages of adsorbates, and surface defects. It is not clearly understood as to whether adsorbate coverages, or the disorder initiated by it, is the dominant cause for surface state formation.

2.3.3 Virtual Gap States / Adsorbate Induced Gap States Model

In this model[7], surface states derive from the complex wavefunctions which become ‘real’ at the surface, due to the altered boundary conditions, as opposed to
2.3. Extrinsic Surface States

bulk conditions. At the surface, the Bloch states, or the virtual gap states split off from the conduction and valence bands, creating real states at the surface. These states create a U-shaped continuous distribution across the forbidden gap (See Figure 2.8), where states closer to the conduction band exhibit acceptor character and states closer to the valence band exhibit donor character. The minimum of this U-shaped distribution is denoted as the charge neutrality level (CNL) where these real states cross over from donor to acceptor character. Upon deposition of an adsorbate onto the surface, and dependant on the position of the CNL, a transfer of charge occurs.

In 1947, Bardeen proposed a charge neutrality condition for surfaces: namely, that the charge held in surface states \( Q_{ss} \) must equal the charge contained in the space charge region \( (Q_{sc}) \)[29]. Mönch[7] refined this approach to include the charge associated with adsorbates \( (Q_{ad}) \):

\[
Q_{ss} + Q_{ad} + Q_{sc} = 0 \tag{2.5}
\]

The position of the Fermi-level can then be calculated by solving for \( e_0|V_s| \) in the following equation:

\[
Q_{sc} = +(2\varepsilon_0 e_0 N_D e_0 |V_s|)^{1/2} \tag{2.6}
\]

The charge transfer between the substrate and adsorbate can be estimated by Pauling's model of partial ionic character for covalent bonds. The charge transfer between an adsorbate and a GaAs substrate can be estimated from:
\[ \Delta q = 0.16 | X_{\text{ad}} - X_s | + 0.035 | X_{\text{ad}} - X_s |^2 \] (2.7)

where \( X_{\text{ad}} \) and \( X_s \) are the electronegativities for the adsorbate and semiconductor substrate, respectively. \( X_{\text{Ga}} = 1.81 \) and \( X_{\text{As}} = 2.18 \), \( X_{\text{GaAs}} = 1.99 \). Depending on the electronegativity of the adsorbate compared with \( X_{\text{GaAs}} \), charge will be transferred away or towards the GaAs surface. For example, \( X_{\text{In}} = 1.78 \), and thus an indium atom donates a charge. Despite the fact that As has a higher electronegativity than GaAs, each surface As atom may contribute to the formation of metallic clusters. Charge balance at metal-semiconductor interfaces is attained when the Fermi-level of the metal coincides with the charge neutrality level. This extension of the virtual gap states model is known as the Metal Induced Gap States (MiGS) Model[30].

2.3.4 Advanced Unified Defect Model (AUDM)

Contrary to the Virtual Gap States model, Spicer et al.[31] proposed the dominant mechanism for Fermi-level pinning is not charge transfer, but defect formation due to adsorbates. They argue that the surfaces of III-V semiconductors become strongly perturbed at sub-monolayer adatom coverages, independent of adsorbate species. Adatoms form defects inherent to the substrate, and form electronic levels at the same predicted positions in the band gap, irrespective of the specific adatom.

Using photoemission spectroscopy they have shown that the Fermi level becomes pinned with as little as 1% Oxygen coverage or 20% metal coverage. Low Energy
2.3. Extrinsic Surface States

Electron Diffraction (LEED) show that surface becomes disordered at these coverages. With thicker oxide coverages, native atoms diffuse through the oxide before they react with ambient oxygen, leaving behind vacancies at the oxide/III-V interface.

Spicer et al. subsequently revised their UDM model and proposed the Advanced Unified Defect Model[8]. In this revision, they specifically identify the dominant defect to be the Arsenic antisite, $\text{As}_{\text{Ga}}$. This acts as a donor, with energy levels at 0.75 eV and 0.52 eV above the valence band maximum, for EL2 and EL2++, respectively. The complementary defect to the $\text{As}_{\text{Ga}}$ antisite is the $\text{Ga}_{\text{As}}$ antisite, which acts as an acceptor in GaAs (See Figure 2.9).

Figure 2.8: Band diagram showing Virtual Gap States and its Charge Neutrality Level. Source: Mönch 1986[7].
2.3. Extrinsic Surface States

Figure 2.9: Schematic energy diagram of defect levels as proposed by the Advanced Unified Defect Model by Spicer et. al[8].

2.3.5 Unified Disorder Induced Gap States (DiGS) Model

Whilst the ViGS attributes Fermi-level pinning to charge balance, and the AUDM the As$_{Ga}$ antisite defect, the DIGS model[9] attributes it solely to surface disorder. Insulator or metal deposition results in a disordered interface layer with the degree of disorder determining the magnitude of the surface state density (See Figure 2.10). Associated interface strain manifests itself in variations in bond length, bond angles, and interface irregularity. This results in a U-shaped surface state distribution with the minima at the hybrid-orbital energy, $E_{HO}$, also known as the transition point from bonding to antibonding states. This corresponds to the pinning energy for the Fermi-level, which is predicted to be at 5.0 eV ± 0.1 eV from the vacuum level for most tetrahedrally coördinated semiconductors, regardless of the particular adsorbate; a
2.3. Extrinsic Surface States

2.3.6 Fermi-level Pinning and Recombination

For an ideal surface with no surface states, the position of the Fermi level with respect to the band gap is identical to that in the bulk. With surface states, the Fermi can become pinned. An n-type semiconductor with electron concentration of $10^{18} \text{ cm}^{-3}$ has a corresponding surface carrier concentration of $10^{10} \text{ electrons cm}^{-2}$. If the density of surface states is $10^{15} \text{ eV}^{-1}\text{cm}^{-3}$, then the Fermi-level energy can move within a band of energy given by the surface carrier concentration divided by the surface state density, which for the example above gives $10^{-5} \text{ eV}$, showing that the Fermi-level is constrained to exist in a very narrow energy band or, is essentially
2.3. Extrinsic Surface States

Occupation of surface states result in a local charge density which is reflected in band bending. The surface band bending can be measured with respect to the Fermi-level in the bulk since the Fermi-level must remain constant from the bulk to the surface, with respect to the vacuum level. The surface band-bending will create a region in which the carrier concentration differs from that in the bulk (where the bands are flat) and is known as a space-charge region.

2.3.7 Surface Recombination Velocity

Surface states can act as traps for minority carriers. Surface recombination velocity is defined as the number of carriers recombining at the surface per unit area per unit time per unit volume of excess carriers at the boundary between the quasineutral and space charge regions \((x=d)\) in Figure 2.11. The Shockley-Reed-Hall expression for bulk recombination, modified for surface recombination, gives the Stevenson-Keyes expression for a distribution of traps of type \(j\) [32]:

\[
S = \frac{R}{\Delta n} = \sum_j N_s j \frac{\sigma_i^j \sigma_p^j n n \nu n (n_o + p_o)}{\sigma_n^j b (n_0 + n_T^j) + \sigma_p^j b (p_0 + p_T^j)}
\]  

(2.8)

where \(N_s\) is areal surface state density, \(\sigma\) is capture cross section, \(n\) and \(p\) are the equilibrium carrier concentrations at the surface, and at traps, as denoted by their respective subscripts. Note that this equation assumes \(n_o + p_o \gg n_1\), where \(n_o\) and \(p_o\) are equilibrium carrier concentrations, and \(n_1 = n_1\) is excess carrier concentration.
Extrinsic Surface States

\( \nu \) is thermal velocity where:

\[ \nu_T = \sqrt{3kT/m^*}. \]  

(2.9)

The SK expression incorporates thermal velocity of the carriers, which may become more of a factor for GaAs, which has disparate carrier mobilities for electrons and holes.

A more intuitive equation that directly relates band bending and surface trap density to surface recombination velocity is the following by Wang which is a modification of the Stevenson-Keyes expression[33]:

\[ \nu_{surf} = \frac{U}{n_1} = \frac{N_t C(p_0 + n_0)/2n_i}{\cosh[(E_t - E_{fi} - e\phi_o)/kT] + \cosh[e(\phi_s - \phi_o)/kT]} \]  

(2.10)

where \( N_t \) is trap density, \( C = \sqrt{C_p C_n} \), where \( C \) is the proportionality constant for electron or hole capturing process, \( E \) is energy of the surface trap level and intrinsic Fermi-level (above the valence band maximum), respectively. The term in the denominator \( e\phi_s \) is a measure of band bending at the surface, i.e. the difference between the Fermi-level at the surface and the Fermi-level in the bulk. \( \phi_o \) is a parameter defining the ratio of \( C_p/C_n \) where

\[ \frac{C_p}{C_n} = \exp\left(\frac{2e\phi_o}{kT}\right) \]  

(2.11)

Physical interpretation of the effect of band bending and surface state density can be easily inferred from equation 2.10. \( \nu_{surf} \) is a maximum when \( e(\phi_s - \phi_o) = 0; \)
2.3. Extrinsic Surface States

that is, when the band bending at the surface equals the ratio of the capture cross sections. (Note, that this does not take into account tunneling through the potential barrier, which would increase in probability with increase in band bending). For a \( \frac{C_p}{C_n} \) ratio of 10, \( e\phi_0 = 0.03 \) eV. For an n-type semiconductor with trap energy near midgap, maximum \( \nu_{surf} \) occurs when band bending is large, when the surface Fermi-level nearly equals the intrinsic Fermi-level. Thus the methods to reduce surface recombination velocity according to equation 2.10, are to either reduce surface trap density, or to alter band bending so as to limit the capture of one type of carrier. Recombination requires the availability of both electrons and holes, and reducing the capture of either one will be the limiting factor. Thus for the n-type semiconductor, a flat band structure, or a strong inversion layer will reduce surface recombination velocity. Untreated GaAs surfaces have \( N_{ss} > 10^{13} \) cm\(^{-2}\)eV\(^{-1}\)[34], and \( \nu_{surf} \) in the order of \( 10^4 - 10^7 \) cm/sec[32], which is dependent on doping concentration and surface preparation.

Peak photoluminescence intensity gives a non-destructive measurement of the surface recombination velocity, making it a main benchmark for passivation. Precautionary measures must be taken when interpreting the data. The danger in using a very high excitation intensity is that all recombination channels will saturate (\( G_o \) term will dominate in equation 2.12) and the emission intensity of a surface with high surface state density will approach that of one with a low surface state density. Peak intensity also varies with excitation wavelength. Using a shorter wavelength exci-
2.3. Extrinsic Surface States

Figure 2.11: Energy-level diagram used in defining the various energy levels for analysing surface effects. $E_t$ is trap energy level, $E_f$ is the Fermi-level and $E_{fi}$ is the intrinsic Fermi-level.

A typical beam results in a shallower penetration of the beam into the semiconductor, thereby exciting carriers only in the vicinity of the surface and space charge region. Carriers bound to surface states causing band bending will be excited and diffuse into the bulk, reducing band bending, and a flatband structure will reduce surface recombination velocity (see Figure 3.6).

Surface recombination velocity can be determined from PL peak intensity. Figure 2.12 shows the relation of PL-intensity increase vs. minority carrier diffusion length and surface recombination velocity. Note that an order of magnitude PL increase can correspond to several order of magnitude decrease in S. Photoluminescence emission can be related to minority carrier diffusion length and surface recombination velocity.
with the following equation taken from Ettenberg[10]:

$$F = \frac{(1-R)G_oL^3}{4\pi\tau_R D} \left( \frac{\beta L + SL/D}{\beta L(\beta L + 1)(1 + SL/D)} \right)$$  \hfill (2.12)

where $F$ is the photoluminescence photon flux, is the $R$ is the reflection coefficient of the excitation laser, $G_o$ is the minority-carrier generation rate, $L$ minority carrier diffusion length, $\tau_R$ radiative lifetime, $D$ diffusion coefficient, and $S$ is the surface recombination velocity, and $\beta$ the absorption coefficient of the excitation laser. Internal absorption of generated photons $\alpha$ is considered much less than $\beta$, and is ignored in this equation (For example using the 532 nm line of an Nd:YAG laser for excitation, $\beta = 7.5 \times 10^4 \, \text{cm}^{-1}$, and for photons generated in GaAs at 1.42 eV, $\alpha = 4 \times 10^3 \, \text{cm}^{-1}$[35]). Minority carrier diffusion length is dependent on the type of carrier, and material quality, and is defined mathematically as:

$$L = (D\tau)^{1/2} \quad \hfill (2.13)$$

$$L^2 = (\mu kT/q)\tau \quad \hfill (2.14)$$

The second relation substitutes the Einstein's relation. Thus minority carrier diffusion length for n-type GaAs would be much smaller than for p-type GaAs, since hole mobility is $\sim$20 times lower at room temperature. Mobilities at room temperature are: $\mu_p = 400 \, \text{cm}^2/\text{Vs}$ $\mu_e = 9400 \, \text{cm}^2/\text{Vs}$ [36].
Figure 2.12: PL enhancement as a function of minority carrier diffusion length $L$, and surface recombination velocity. Source: Ettenberg 1975 [10]
Part II

Literature Review
Chapter 3

Previous Passivation Attempts

3.1 Dry versus Wet, Baking versus Poaching

The field of GaAs surface passivation has now become a mature area. Virtually every possible candidate for passivation has been attempted by using either a wet or dry process. Of the two approaches dry processing is preferred as it yields more repeatable, if not superior, results due to the stricter control of processing conditions, and reduced sources of contamination. The transition from wet to dry processing is inevitable; a dry process has numerous advantages over wet. Wet processes are principally limited to aqueous solutions of chalcogenides or chlorides - a dry process has practically no limitations on the material selected for deposition. Furthermore, with a wet process, thickness of the film deposited is difficult to control to significant accuracy. Often a wet process will only saturate the dangling bonds of the surface;
incomplete submonolayer coverages and instability of bonding will lead to reoxidation of the surface. Also, further processing is usually required after passivation (metallization, dielectric mirror deposition), and a dry process offers the advantage of keeping the device in vacuum, avoiding reoxidation and impurity incorporation.

This review will briefly cover wet passivation (for a more comprehensive review see Edirisinghe, 1997[37]). In situ methods using varying deposition techniques and adsorbates are discussed for GaAs(100) and GaAs(110) surfaces. Due to the immense of amount of research on GaAs surface passivation, only previous work that I considered significant is discussed. Some of the passivation treatments are omitted include ZnSe passivation, nitridation of surfaces, and plasma passivation with NH₃ or H₂. The reasons for these exclusions are the following: plasma passivation is discussed in detail by Aydil et al.[34], and as of yet, has not demonstrated any significant results. ZnSe-GaAs(110) interface is actively being studied, but more for blue laser diodes (see for example, [38]), as is GaN.

3.2 Photowashing

One of the simplest methods of wet passivation involved not the deposition of an adsorbate, but the removal of the elemental arsenic and arsenic oxides by photowashing[11][39]. This involved submersing the sample in flowing ultrapure water and irradiating the surface with a 532 nm laser. A tenfold PL enhancement was observed after five minutes of processing, but once the sample flow of water was ceased, degradation back
Figure 3.1: Real time PL spectra showing effect of photowashing; and instability after washing is stopped. Source: Kaufman et al. 1991[11].

to near original conditions were observed after only about 1/2 hour (see Figure 3.1), and was accelerated in the presence of excess oxygen. Further PL enhancement may be limited by the insolubility of the Ga$_2$O$_3$, where culprit As atoms may be entrained as depicted in Figure 2.1. Though no long term passivation scheme was developed, photowashing experiments of these kinds gave further experimental evidence to the deleterious effects of arsenic oxides.
3.3 Chalcogenides: Temporary Transcendence

The earlier attempts at passivation involved aqueous treatment of the surface by solutions of Na₂S or NH₄S spin coated onto a surface ex situ. Excellent properties approaching that of a AlGaAs/GaAs interface were obtained using a Na₂S/Se process[40]. Despite the large photoluminescence gains reported, the films were thermodynamically unstable in air, showing a decrease in performance with time[41], and were reoxidized after a few hours[42]. In addition, they left behind a yellow crusty residual film[43]. It was initially proposed that the photoluminescence enhancement originated from reduced band bending, but experiments showed that the Fermi level was closer to the valence band maximum for n-type GaAs, indicating increased band bending. This contradiction led to further understanding of recombination mechanism at the interface. The increase of band bending was due to the reduced ratio of the As₉Ga antisite defect to its compensating acceptor, the Ga₆₉ antisite defect[8]. This additional band bending created a potential barrier for minority holes, preventing recombination at the surface, and increased photoluminescence[44] (as predicted by equation 2.10).

The passivation instability of aqueous sulfidation of GaAs surfaces can be explained by X-ray Photoelectron Spectroscopy (XPS) spectra and ab initio calculations. XPS spectra show that As3d and Ga3d core level shifts only occur if some kinetic barrier is overcome; that is, the sulphur will only physisorb without the assistance of heat, or laser energy, or sulphur excitation[13]. In the model of Ping
et al.[45], sulphur incorporates itself into the surface in between a Ga dimer. This incorporation involves the breaking of this Ga dimer bond, which can explain the kinetic barrier for chemisorption over physisorption. And, the mechanism of sulphur passivation is that it pushes the surface Ga atoms to their ideal bulk positions, pushing the gap states towards the bands. Synchrotron radiation shows that not all sulfur is bound to the surface; S-S bond exist, and these disappear after heating to 250°C[43].

This instability was addressed by encapsulating the sulfidized surface with a mechanically strong dielectric (see for example, [12]) that would prevent interaction
of the ambient and outdiffusion or desorption of sulfur. Various dielectric deposition methods were compared on (NH₄)ₓSₙ-treated GaAs, including Plasma Enhanced Chemical Vapor Deposition (PE-CVD), sputtering, pyrolytic CVD, and ECR-CVD. All the processes except ECR-CVD, showed a degradation in PL intensity from the uncapped sulphur treated surface. The sputtering, and CVD processes using rf-plasma, have high ion energies which bombard the surface to induce surface damage, and rendered the surface back to equivalent its original untreated electrical state. ECR-CVD involves ion energies of 10-20 eV, and SiN and SiO₂ deposition on the passivated sulfidized surface showed a slightly further increase in PL intensity. The degradation incurred by the high energy processes not only gives indication of the sensitivity of sulphur passivation and semiconductor surfaces to plasma processing, but indicates the potential benefit of using ECR plasmas for surface treatment. Though even with an Si₃N₄ cap on NH₄S passivated surfaces, the benefits degraded under high-incident light power density \( P_o=1060 \) W/cm²[46], making this process unsuitable for high power laser diode passivation.

The limitations of aqueous sulfidization of surfaces were addressed by depositing a GaS film on the surface, in a MOCVD or MBE process[47][48][49]. The salient advantage of using these processes over aqueous sulfidization is the ability to deposit the compound GaS: GaS the most stable phase in the Ga-As-S ternary system[50]. In an aqueous process both Ga and As sulfur compounds are formed and leads to further arsenic formation at the substrate from the decomposition of the As₂S₃ com-
3.3. Chalcogenides: Temporary Transcendence

Figure 3.3: TEM Micrograph of a cross section of SiO₂ deposited on GaAs by remote plasma chemical vapor deposition at 125°C. Source: Shin et al. 1990[13].

pounds (As₃d As-S peak disappeared upon heating sample to 400°C). Furthermore, limitations of kinetic barrier, submonolayer coverages, impurity incorporation are eliminated by dry processing. Using GaS as a passivant not only serves the function of bond saturation by sulphur termination, analogous to a wet process, but there is the added benefit of a thick protective film, which was grown as thick as 400 nm, which also obviated the need for a capping layer. By depositing thicker films, carrier confinement is realized since the band gap of GaS was determined to be approximately 4.0 eV, having a valence band offset with GaAs of 1.9 eV. Films were deposited using either a MOCVD process with a [(t-Bu)GaS]₄ precursor, or by thermal decomposition of Ga₂S₃ in a Knudsen cell. These epitaxial, thicker films resulted in PL enhancement by two orders of magnitude, with negligible degradation after four months exposure to air. Interestingly, they report that the PL degradation was not
related to film thickness, possibly due to a naturally forming outer layer of Ga$_2$O$_3$ acting as a diffusion barrier. This is expected as predicted from the free energies of these compounds ($\Delta G_{Ga_2O_3}^= = -998.3\, KJ/mol, \Delta G_{GaS}^= = -209.2\, KJ/mol$). Films exhibited excellent electrical properties, with interface state density determined to be $9 \times 10^{10}\, \text{cm}^{-2}\text{eV}^{-1}$[51].

More recently, further reduction in the interface state density maximum was reported for GaS passivations using the same precursor $[(t-\text{Bu})\text{GaS}]_4$[14]. The authors report a minimum interface state density of $5.0 \times 10^{10}\, \text{eV}^{-1}\, \text{cm}^{-2}$ near midgap by C-V measurements. This half order of magnitude reduction in interface state density as compared to GaS deposited by a MOCVD process is attributed to a salient advantage of the MBE process: surface reconstructions can be defined prior to passivation. The arsenic-rich c(4×4)As reconstruction showed the greatest PL enhancement of approximately 75 times, and the (2×4)As structure only showed an enhancement of ~40 times, with corresponding interface state density of $1.8 \times 10^{11}\, \text{eV}^{-1}\, \text{cm}^{-2}$. The authors postulate that the superiority of the c(4×4)As reconstruction for GaS passivation is that excess arsenic at that surface may desorb and form a sharp As-GaS interface. Partial As-coverage reconstructions, such as (2×4)As were believed to promote Arsenic vacancies at the passivated interface. The c(4×4) surface was also found to be more suitable for passivation as compared with a (2×4) surface, when using a silicon interface control layer, where little PL enhancement was observed for (2×4) surfaces[15].
Figure 3.4: Interface state density as a function of band gap position and surface reconstruction prior to sulphur deposition. Source: Okamoto et al. 1998[14].
3.4 Phosphorus: Combustible but effective

Another high partial pressure element was attempted for passivation: phosphorous. Olego et al. [52] was the first to passivate GaAs surfaces with phosphorous in an MBE chamber. They selected it for candidacy due to its unique properties when deposited at temperatures below 200°C: it formed an amorphous polymeric structure with few dangling bonds. Using <111> wafers, phosphorous was deposited at room temperature and surface recombination velocity, determined by room temperature PL enhancement, was estimated to have decreased by an order of magnitude. Deposition in an MBE chamber is messy, with phosphorous build-up on the walls, which poses the danger of unintentional doping and spontaneous combustion upon exposure to atmosphere.

Since the work of Olego et al., there were few reports of further work on phosphorous passivation, and most reports concentrated on sulfur treatments. It was not until the early nineties that further publications on phosphorous passivation began to appear again. This coincided with the widespread use of MOVPE/MOCVD for III-V phosphide-optoelectronic devices, and presented a technique which is far more amenable to phosphorous processing.

The importance of a low defect surface and the selection of deposition sources was shown to be crucial for phosphorus passivation. Satisfactory room temperature PL enhancement was reported, by Viktorovitch et al., by MOVPE treatment of ex situ GaAs(100) wafers using phosphine vapor (PH₃) [53]. XPS spectra showed that
3.4. Phosphorus: Combustible but effective

the phosphine simultaneously removed native oxides above 350°C, and reacted with the surface via As/P exchange mechanism to form a thin superficial layer of GaP. GaP has favorable properties required in a passivation layer: large energy gap of 2.27 eV (indirect), and a smaller lattice constant (a₀=5.45 Å) than GaAs, requiring the overlayer to be sufficiently thin. Optimum reaction temperature was determined to be between 550°C and 570°C which resulted in only a PL enhancement of four times. Years later, Harrison et al. reported a large photoluminescence gain using tertiaobutylphosphine(TBP) vapor in an MOCVD process[54]. They too, did not etch or rinse the wafer before loading into the chamber, though their surface was an MBE grown surface rather than a mechanically polished substrate. A 300× gain in room temperature photoluminescence was reported over samples that were held in atmosphere for one year, and 100× over a sample that was restored by tertiaobutyllar-sine(TBA). Low temperature spectra at 1.6K show an enhancement of the A°X and D°X transitions, indicating less surface recombination. The dramatic improvement from using Harrison’s treatment as compared with Viktrovitch’s can be explained from the initial and processing conditions. In both cases the process temperature and treatment time were 550°C and 10 minutes, respectively. The reason for the dramatic difference in performance can be attributed to the higher quality starting substrate (MBE versus mechanically polished), and a lower processing pressure (0.1 torr vs. atmospheric pressure), and the use of a precursor with lower decomposi-tion temperature (TBP vs. PH₃). The reasoning is as follows: the higher defect
density in the mechanically polished substrate would limit the benefits imparted by the GaP overlayer, since a large proportion of the non-radiative recombination channels through defects will remain largely unchanged; a lower background pressure would prevent oxygen or other impurities to incorporate into the film; and at 550°C, more phosphorous is dissociated from the precursor (\(\sim 90\%\) TBP, \(\sim 10\%\) PH\(_3\)[55]). A larger percentage of phosphorous can be dissociated from PH\(_3\) using a higher substrate temperature, but deposition temperature above 550°C resulted in reduced PL intensity[53], which was attributed to incongruent melting and/or the reactivity of the hydrogen.

The use of III-P compounds with a different lattice constant than GaAs requires the superficial layer to be sufficiently thin, and this was explained by Wada et al.[56], where they coin the term “atomic layer passivation”. In their approach to passivating GaAs, they deposited an ultrathin layer of InP, in an MOCVD process using tri-methly-indium (TMI) and PH\(_3\) precursors. They stress the importance of passivation layer to be less than 20-40 Å, since the lattice match offset can create strain-induced defects at thicker coverages. Another reason given for atomic layer coverages is to sufficiently quantize the layer preventing any bound states in the gap, and also to impart biaxial compressive stress, to further increase band offsets, since the bandgap of InP is 1.34 eV. Interestingly, a reduction in band-bending by 0.3 eV was observed (by As3d and Ga3d core level spectra) for the ultrathin 10 Å InP layer, but reverted to the original band configuration at thicker coverages, as corroborated
3.5 Silicon: If only GaAs were as lucky

The immense commercial success of silicon devices may be attributed, in part, to the nearly ideal interface formed with its oxide. Silica(SiO$_2$) forms a mechanically strong, inert, hermetic, stress free layer with silicon, and at the same time, and more significantly, has a very low interface state density of $1.0 \times 10^9$ eV$^{-1}$ cm$^{-2}$. It was initially proposed by Hasegawa et al.[57], to take advantage of this ideal interface by passivating GaAs with an ultrathin layer of silicon[58], followed by an encapsulation with SiO$_2$ or Si$_3$N$_4$(See Figure 3.5). The apparent shortcomings of lattice mismatch ($a_o$(Si) = 5.43 Å $a_o$(GaAs) = 5.65 Å) and smaller bandgap of silicon were overcome by growing less than 10-15 Å (i.e. 2-3 monolayers), thus forming a pseudomorphic interface and quantizing silicon states. According to their own DIGS model, a thin silicon interface control layer (ICL) is a good candidate to restore some order at the GaAs surface, due to its good bond matching.

The energy band offsets are an important factor in obtaining passivated surfaces. No Fermi-level pinning was reported for silicon on In$_{0.53}$Ga$_{0.47}$As surfaces, since the band gap difference prevented any conduction or valence band derived states from entering the In$_{0.53}$Ga$_{0.47}$As gap, which was determined by C-V measurements. It is important to note that these properties were only realized after annealing for 1 hour at 350°C. The Si band offset with GaAs is not as large as it is with InGaAs, and silicon
3.5. Silicon: If only GaAs were as lucky

Conduction band derived states were found to be in the GaAs band gap, pinning the Fermi-level. In a later paper[59], the same authors attribute the non-uniformity and insufficient quantization of the Si-ICL on the intermixing effects incurred by the ArF excimer (193nm) photo-CVD dielectric deposition. They counter by Si deposition at a lower temperature (300°C vs. 500°C) and nitridation at room temperature of the outer monolayer with low energy ECR-plasma. Though no electrical characterization was performed, photoluminescence enhancement of about 50% over an unpassivated clean MBE surface in UHV was realized with just the silicon overlayer, and more so with the Si/Si$_3$N$_4$ stack. The nitridation of the outer layer demonstrated that this layer is indeed crucial, so as to form a quantum well, in order to increase the band gap of silicon and blueshift bound defect states out of the forbidden gap.

Having a layer as thin as possible is required to blueshift the conduction band minimum (CBM) in order for the small gap of Si (1.1 eV) to straddle the gap of GaAs (1.4 eV). Conventional quantum theory predicts the CBM increase is inversely proportional to $d^2$, where $d$ is the thickness of the quantum well. More advanced quantum confinement theory though, predicts quantum confined Si to scale with size $1/d^\gamma$, where $\gamma=1.2$ to 1.8[60]. Synchrotron Si L-edge absorption spectra for Si in an asymmetric well determined that the value for $\gamma$ is approximately 1.7, and the CBM blueshift can be estimated by the following equation[61]:

$$\Delta E_{CBM} = \frac{0.15}{d^{1.7}}$$ (3.1)
3.5. Silicon: If only GaAs were as lucky

Figure 3.5: Schematic diagram of Si-Interface Control Layer passivation technique. (a) Insufficiently thin Si layers results in weakly quantized bound states in mid gap. (b) Ultra-narrow silicon layer shifts states out of the band gap. (c) Cross-sectional view of the Si-ICL passivation heterostructure. Source: Mutoh et al. 1999[15].
3.5. Silicon: If only GaAs were as lucky

Though experimentally it was found that a 0.3 nm Si film blueshifted the CBM ~0.47 eV and that the film should be thinner than 2.5 nm for any quantization. An additional benefit is that silicon becomes luminescent at these dimensions, and if used to passivate laser diodes, any carrier leakage into this film will not contribute to heating.

Laser diodes passivated with an ultrathin layer of silicon sandwiched on the other side by Al₂O₃ were shown to improve properties and mitigate COD[62]. Silicon was deposited on in situ cleaved facets, at room temperature, which explains the relatively minor room temperature-PL enhancement: at these deposition temperatures, the film is amorphous. It is believed that the tail states of amorphous silicon and defect states contributed by microvoids and vacancies, associated with room temperature processing, contribute states to the midgap[63]. This claim was supported from the fact that some of these states were pushed out of the midgap after annealing. States created by the step-laden facets inherent with the cleaving process[64] may also create additional states in the gap. This claim has validity due to the fact that seven of the ten lasers survived the stress test.

Scanning tunneling microscopy/spectroscopy (STM/STS), gave further insight into the Si/GaAs(110) interface. Atomic resolution band structure was obtained by \( \frac{d\ln I}{d\ln V} \) spectra and it was shown that at perfectly ordered atomic sites, no band bending was observed, but spectra taken at step edges, and near gallium vacancies show a shift in the Fermi level 0.4 eV more towards mid gap, on \( n^+ \) cleaved surfaces[65][66].
3.6. $\text{Ga}_2\text{O}_3$ is to GaAs as $\text{SiO}_2$ is to Si?

More fascinating, though, are spectra taken between two silicon islands; STS spectra showed a downwards shift in the Fermi level, which was similar to spectra taken on top of an island, suggesting that silicon has electrical influence beyond its dimensions, into the surrounding GaAs substrate.

Despite the excellent results obtained, the drawbacks to silicon passivation include the following: monolayer thickness for sufficient quantization, and the need for a dielectric on the opposite side for potential well barriers on either side.

3.6 $\text{Ga}_2\text{O}_3$ is to GaAs as $\text{SiO}_2$ is to Si?

It is well established that unlike silicon, the naturally formed oxide, namely the arsenic oxide, is the culprit responsible leading to high surface state density. Thus an oxide film consisting only of $\text{Ga}_2\text{O}_3$, should be innocuous, or possibly even beneficial. Attempts at controlled oxidation of the surface by thermal means, found that arsenic related oxides will grow as well. Earlier attempts at $\text{Ga}_2\text{O}_3$ growth, showed that negligible improvement was realized by radio frequency-plasma oxidation of gallium evaporated using an e-beam[25]. Electrical property enhancement was most likely due to the rf-plasma nitridation prior to gallium oxide deposition. The plausibility of surface damage by ion bombardment is highly likely, even though they used plasma parameters below sputtering threshold, since ion energies for rf-plasma are in the order of keV. Similar properties were obtained earlier with $\text{GaO}_x\text{N}_y$ graded structures by thermal decomposition of ammonium-gallium tribromide complex in oxygen[67].
The benefits of Ga$_2$O$_3$ passivation and the importance of processing conditions were demonstrated by the excellent electrical and optical properties of the Ga$_2$O$_3$-GaAs(100) interface reported by Passlack et al.[24]. Interface state density in the low $10^{-10}$ eV$^{-1}$cm$^{-2}$ was determined by C-V measurements, close to the near ideal interface of Al$_{45}$Ga$_{55}$As-GaAs ($2 \times 10^{-9}$ eV$^{-1}$cm$^{-2}$) and PL enhancement of two orders of magnitude over an untreated air-exposed surface was attained. The results from this process demonstrated the excellence of Ga$_2$O$_3$ passivation (other large bandgap oxides were tested (MgO, SiO$_2$), but did not result in any PL enhancement), and stressed the importance of dry processing conditions. Ga$_2$O$_3$ was deposited on MBE grown As-rich ($2 \times 4$) surfaces, which prior to deposition, was exposed to a maximum of 10-100 L (1 L=10$^{-6}$ Torr·sec$^{-1}$) of residual chamber gases. This was made possible by using a UHV chamber, where during sample transfer the background pressure was in the range of $10^{-10}$ Torr. The method of deposition involved the e-beam sublimation of a Gd$_3$Ga$_5$O$_{12}$ single-crystal (since single crystal Ga$_2$O$_3$ was unavailable), where minimal Gd evaporation was expected due to the high boiling point of Gd$_2$O$_3$ (4000 K). RBS measurements detected as much as 1.5 at% in the film[46]. Ex situ surfaces did not show as much of an enhancement. Carbon impurities on air-exposed surfaces were deemed the culprit, where even by thermal desorption at 580-600°C, and subsequent passivation, interfaces could not equal those of surfaces passivated in situ (This wafer preparation method was found to have residual carbon concentration of $10^{19}$cm$^{-3}$[27]). Nevertheless, excellent minimum surface state density was reported.
3.6. $\text{Ga}_2\text{O}_3$ is to GaAs as $\text{SiO}_2$ is to Si?

![Figure 3.6: Photoluminescence intensity versus excitation wavelength for $\text{Ga}_2\text{O}_3$-GaAs structures, using $\text{Al}_{0.45}\text{Ga}_{0.55}\text{As}$-GaAs interface as a reference point. Source: Passlack et al. 1995[16]](a)

in the upper $10^{10}$ eV$^{-1}$cm$^{-2}$ range, with corresponding $S=9000$ cm/sec[68].

$\text{Ga}_2\text{O}_3$ films were proven to be thermodynamically more stable than sulfur passivation capped with a dielectric. Rapid thermal annealing (RTA) at 1000°C for 30 sec of samples capped with SiO$_2$ were used to study the film stability. XPS interfacial profile showed that the bonding configuration of As and Ga remain unchanged, that is, no arsenic oxides were formed. Corresponding PL measurements, though, show a degradation in peak PL intensity of 21%. However, samples that were RTA’ed at 700°C to 800°C did not show any degradation of peak intensity;
3.6. $\text{Ga}_2\text{O}_3$ is to $\text{GaAs}$ as $\text{SiO}_2$ is to $\text{Si}$?

Transmission Electron Microscopy (TEM) cross sectional micrographs of these RTA samples showed interfaces to be planar on the nanometer scale. In fact, $\text{Ga}_2\text{O}_3$ films became polycrystalline through annealing, and resisted etching in concentrated HF. This is in contrast to silicon passivation, where intermixing at the interface was witnessed with growth temperatures as low as 500°C. Long term stability at high powers was demonstrated by excitation at high incident power density (1060 W/cm$^2$) (see Figure 3.7), where the films exhibited virtually no degradation – even the films which underwent severe RTA at 1000°C, whereas surfaces passivated with NH$_4$S and capped with Si$_3$N$_4$ degraded by almost an order of magnitude during the first hour of high-intensity excitation.

In addition to the superior stability and electrical properties of $\text{Ga}_2\text{O}_3$, optical properties of these films provide an ideal front facet coating. $\text{Ga}_2\text{O}_3$ has a large bandgap (4.4 eV) and a refractive index of 1.841-1.855\cite{24} is almost the exact square root of $n_{\text{GaAs}}=3.6$, making it ideal for antireflective coatings. Reflectivity at dielectric interface with film thickness $\frac{1}{4} \lambda$ can be calculated by the following equation:

$$R = \left[ \frac{n_s - n_L^2}{n_s + n_L^2} \right]^2$$ \hspace{1cm} (3.2)

where $n$ is the refractive index, and subscripts $S$ and $L$ refer to substrate and the thin film overlayer, respectively. Absorption of $\text{Ga}_2\text{O}_3$ at the EDFA pump wavelength of 980 nm was measured to be as low as 100 cm$^{-1}$ giving a front facet reflectivity of 1%. Having a low front facet reflectivity and high back facet reflectivity is crucial for
Figure 3.7: Photochemical stability of GaAs(100) passivated with Ga$_2$O$_3$ compared to a sample that underwent thermal stress, and a (NH$_4$)$_2$S passivated capped with a dielectric. Source: Passlack et al. 1996[17]

maximum external quantum efficiency[69]. The combined advantage of ideal optical constants, low interface state density, and stability were the reasons these lasers did not undergo COD; they were limited by thermal rollover, and repeated thermal rollover did not result in degradation of output versus current characteristics[70].
3.7 Summary and Commentary

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<th>Summary of Previous Dry Passivation</th>
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<td><strong>Passivation Chemical</strong></td>
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Table 3.1: Summary of various passivation techniques

3.7 Summary and Commentary

All the aforementioned passivation techniques have displayed marked improvement over as-is surface, and interface quality has approached that of a GaAs-AlGaAs interface. The selection criteria should then focus on other factors. InP, and SiSiN both require ultrathin layers for sufficient quantization so as to not introduce additional states into the bandgap. In fact, Si-SiN4 interface requires the Si3N4 capping layer, or else little or no PL enhancement is observed[15]. Photochemical stability has not been tested with phosphorous nor GaS overlayers, however aqueous sulfidization results and Gibbs free energy values of sulfur compounds indicate that these are not the most stable compounds and would degrade under more aggressive conditions. This leaves Ga2O3, which satisfies all the requirements.

Ga2O3 is an ideal passivation material since it meets all pertinent requirements. It is has a very low interface state density, it is stable, electrically compatible for n-type and p-type doping, and has a large band gap which requires no capping layer. In
effect, Ga$_2$O$_3$ acts simultaneously as a passivation and capping layer, which obviates the requirement of ultrathin layers for passivation effectiveness, or ultrathick to provide sufficient diffusion barrier. In fact, bulk $\alpha$-Ga$_2$O$_3$ density is 6.0 g/cm$^3$[71], and by e-beam deposition, densities as high as 80% were achievable[24], which is still higher than SiO$_2$(2.2 g/cm$^3$) or Si$_3$N$_4$(3.1 g/cm$^3$). These superior properties warrant further investigation into GaAs-Ga$_2$O$_3$ interfaces. However no detailed study has been performed on GaAs(110)-Ga$_2$O$_3$ interfaces, which is of great technological importance, especially for optoelectronic device applications.

It is important to note that the studies mentioned in this literature review were generally not necessarily aimed at understanding the effects various passivation materials GaAs(100) surfaces, but rather to outline the advantages and disadvantages of each process, irrespective of surface orientation. The reason is that passivation studies on (100) surfaces often can not be used to deduce behaviour for (110) surfaces. Unfortunately studies of passivation with respect to surface orientation are sparse, and the effect of the aforementioned passivation candidates have not yet been determined on surfaces other than GaAs(100), except through empirical, indirect data from laser-diode performance. This thesis, in addition to introducing a novel process, aims to provide direct evidence of the mechanisms of surface passivation for GaAs(110).
Part III

Experimental
Chapter 4

Apparatus and Procedure

4.1 UTEMG-1 System

The UTEMG-1 is a custom designed system that consists of four main chambers, two growth chambers, and two characterization chambers which are connected through a common analysis chamber. The analysis chamber can analyze samples using Auger electron spectroscopy (AES), and Ultraviolet Photoemission Spectroscopy (UPS). The other characterization chamber contains an Omicron Scanning Tunneling Microscopy (STM), used for atomic resolution surface microscopy. The main growth chamber, is a Molecular Beam Epitaxy chamber having standard III-V growth and doping Knudsen-cells (K-cells), including Ga, As, In, Al, Si, and Be K-cells. The fourth chamber is the process chamber. All these chambers are interconnected, thereby allowing in situ characterization and processing.
Figure 4.1: UTEMG-1 Custom designed MBE System, comprising of MBE, STM, Analysis, and Process Chamber.
4.2 Process Chamber

The process chamber is a custom designed chamber and is used for surface treatment and dielectric deposition. Currently installed is a Ga evaporation K-cell, and an electron cyclotron resonance plasma gun. There is a $\frac{3\frac{3}{4}}{4}$" port empty, which can be loaded with a low temperature K-cell, or an e-beam evaporation cell. The two K-cells are at a 25° angle to the vertical centre axis, and the ECR-plasma gun is at a 20° angle. Deposition rate and thickness of the Ga is monitored by a Maxtek quartz oscillator (Maxtek TM-100). Note, that this is only used as a rough guide since the precision is low due to the large geometrical offset of the sensor and the centre of the beam flux, and in addition, the sensor decreases in sensitivity with increasing material coverage.

The ultimate base pressure of this chamber is $2 \times 10^{-9}$ Torr, which is the ultimate pressure of a Balzers TPU240 turbomolecular pump backed by a rotary-vane mechanical pump. The turbopump is attached to a conical elbow to limit its conductance, and, when cleaving, to prevent the rejected piece from entering the pump rotors. Conductance is intentionally reduced so as to not require excessively high gas inlet rates to maintain high pressure during plasma processing.

Chamber pressure is measured with an ion gauge, and gaseous species are identified by an SRS Residual Gas Analyzer (RGA) (SRS RGA-300).
4.3 Experimental Procedure

Commercially available GaAs(110) wafers were obtained from American Xtal Technology. These 2" diameter wafers were cut into smaller pieces (~1.5 cm × 1.5 cm) and Indium soldered onto molybdenum sample holders.

Once in the process chamber, the sample was outgassed at 100°C overnight. Before Ga$_2$O$_3$ deposition, surfaces were cleaned in situ. It has been shown that native oxides and organic contaminants can be selectively removed from GaAs surfaces by ECR hydrogen plasma leaving a clean well ordered surface[72]. After twenty minutes of room temperature ECR hydrogen plasma treatment at 1 torr, in situ XPS detected no Arsenic oxide. The removal of these oxides follows from:

\[
\begin{align*}
As + 3H & \longrightarrow AsH_3 & \Delta G^\circ = -130\frac{kcal}{mol} \\
As_2O_3 + 12H & \longrightarrow 3H_2O + 2AsH_3 & \Delta G^\circ = -580\frac{kcal}{mol} \\
Ga_2O_3 + 4H & \longrightarrow Ga_2O + 2H_2O & \Delta G^\circ = -142\frac{kcal}{mol}
\end{align*}
\]

Gallium oxide is more stable than the arsenic oxides, and is reported to be removed after several hours at room temperature. At 200°C, under ECR hydrogen plasma it is reported that Ga$_2$O$_3$ is removed by the formation of the volatile gallium monoxide[73]. With increasing temperature the process is accelerated. Using rf-plasma, however, it is reported that Gallium oxide removal is only possible at a sample temperature of 530°C[34]. Another alternate hydrogen radical supply method
is using a 1600°C W-filament cracker, though this method has high ion energies and increased roughness was observed by using this method[27]. It is definitely favorable to use a lower processing temperature, to prevent diffusion of species near the surface. Effects of hydrogen ECR plasma cleaning on substrates was demonstrated by improved properties of MBE grown GaAs grown on ECR cleaned wafers over normal thermal cleaning[74].

In this thesis, samples were treated under the following conditions: temperatures ranging from 25°C to 300°C for a duration of 30 to 120 minutes; hydrogen pressure of about $5 \times 10^{-4}$ Torr with microwave power of 30-40 W. The ECR plasma has very low ion energies (10 eV–30 eV) at a power of 100 W, ion energies are at the lower end of the range. Low ion energies ensures that minimal surface damage is incurred, as compared to rf-plasmas which have ion energies in the order of keV. During cleaning, other gases are at a partial pressure below $10^{-10}$ Torr, with only trace amounts of water detected at a partial pressure of about $2 \times 10^{-6}$ Torr (see Figure 4.2).

During the cleaning, the Ga cell is heated to 775°C corresponding to a beam equivalent pressure of $1.8 \times 10^{-5}$ Torr (Calculated from [71]).

Once the cleaning is complete the sample is rotated away from the flux. The gas is then switched over to Oxygen, the plasma ignited, with Oxygen pressure of $5 \pm 2 \times 10^{-5}$ Torr, and power of $30 \pm 5$ W. The shutter for the Gallium cell is opened and the sample is rotated downwards, perpendicular to the Oxygen plasma, at 20° to the Ga flux. Several seconds are required to purge the ECR plasma of the Hydrogen,
Figure 4.2: Residual Gas Analysis Scan during hydrogen ECR plasma cleaning of the substrate

and to stabilize the Oxygen plasma; unintentional Oxygen uptake is calculated to be less than $10^3$ L (20 seconds exposure at $5.0 \times 10^{-5}$ Torr) (1 Langmuir=$1 \times 10^{-6}$ Torr sec). According to Spicer et al.[31], this corresponds to less than a 0.2 eV shift in Fermi-level for n-type wafers, and none for p-type, or less than 0.1 ML of oxygen (See Figure 4.3). During deposition, carbon dioxide, or nitrogen is undetectable in the feed gas, therefore less than $10^{-10}$ Torr.
4.3. Experimental Procedure

Figure 4.3: Oxygen uptake on GaAs(110) using unexcited oxygen at room temperature. Source: Mönch 2001[3].
Part IV

Results and Discussion
Chapter 5

Untreated GaAs(110) wafers

5.1 X-ray Photoelectron Spectroscopy

Bonding in the native oxide was investigated using XPS. Normal-incidence monochromatic spectra show two distinct peaks corresponding to the underlying substrate and the native oxide. The As3d signal corresponding to the oxide, with peak at around 44 eV shows that arsenic oxides consist primarily of \( \text{As}_2\text{O}_3 \), as expected from thermodynamic phase diagrams (See Figure 2.7 and Table 2.1). \( \text{As}_2\text{O}_5 \) having binding energy of 45.7 eV, is not detected. The presence of elemental arsenic is difficult to detect, since it overlaps with the As3d signal of arsenic bonded with gallium. Gallium oxide is detected at 20.2-20.8 eV, suggesting suboxides (\( \text{Ga}_2\text{O}, \text{GaO} \)) or \( \text{GaAsO}_4 \) compounds. The double peak for the As3d core level spectra is the spin orbit splitting, with binding energy separation of 0.69 eV. Ga3d spin orbit splitting was not
Table 5.1: Binding energies of Ga3d and As3d core level spectra of an as-is surface, monochromatic source, PE=48 eV. Values in brackets denote binding energy shift discernable.

Ga3d and As3d core level spectra indicate band bending for the doped substrates. Core level spectra are 0.2 eV higher for Si-doped n type GaAs, suggesting an accumulation regime at the surface. Accumulation is also found for the Zn-doped p type wafers, whose core level energies decrease 0.2 eV, indicating band bending to a higher potential energy at the surface.
Figure 5.2: As3d core-level spectra of as-is p-type GaAs(110) surface

Figure 5.3: Ga3d core-level spectra of as-is n⁺ doped GaAs(110) surface
5.2 TOF-SIMS

Time of flight secondary ion mass spectroscopy shows a large proportion of impurities throughout the native oxides. Carbon is detected nearly on a 1:1 ratio with arsenic throughout the oxide, and is not detectable in the substrate. Zinc is used for doping, and a significant amount was found to be in the oxide, supporting the model of substrate consumption during oxidation, as opposed to outdiffusion of Ga and As atoms. Despite the high doping level ($10^{19}$ cm$^{-3}$) sensitivity of Zn by SIMS when in the GaAs lattice renders it undetectable, due to the low ionization efficiency of Zn in GaAs[75].
Figure 5.5: TOF-SIMS depth profile of the native oxide of p-type GaAs(110). Ga spectra intentionally left out for higher resolution of other species.
Chapter 6

Gallium Oxide Passivation: Chemical and Structural Characterization

6.1 XPS Depth Profile

The bonding configuration of the film and the interface were investigated by X-ray Photoelectron spectroscopy (See Figure 6.1). An XPS depth profile was performed with an Al Kα (1486.6 eV) source, at a 90° take-off angle (PE=192 eV), and a fine sputter rate (2x2 mm² raster, 3.5 kV Argon), estimated to be 1 nm/cycle, shorter than the photoelectron escape depth of 2 nm. The first onset of As3d core level spectra show that bonding is exclusively as GaAs; there are no detectable peaks at
6.2. XPS Oxide Analysis

higher energies as expected for As₂O₃ (44.7 eV) or As₂O₅ (45.7 eV), ruling out the possibility of elemental Arsenic formation at the interface from reaction with the substrate. The predominant oxide found on the ex situ surface was As₂O₃, and the absence of this signal suggests that this oxide was completely removed by hydrogen ECR plasma treatment. Ga₃d core level spectra show two peaks at 18.9 eV (Ga bonded as GaAs) and 21.1 eV (Ga bonded to Oxygen). Ga₃d spectra at the interface is fitted as the sum of these two components. The reported value of Ga₃d Ga₂O₃ here is in agreement with values reported by e-beam deposition of 21.2 eV for in situ surfaces, and 20.8 eV for ex situ surfaces[46], corresponding to a peak shift of 2.0 ± 0.2 eV to higher energies. Carbon was only detected in the scans in the outer layers – originating from exposure of the substrate to atmosphere – and undetectable after a few subsequent sputter cycles.

6.2 XPS Oxide Analysis

Ga₃d core level binding energy of the deposited Ga₂O₃ was measured for samples under a range of deposition temperatures. These energies were normalized against C₁s spectra, to correct for sample charging. Table 6.1 lists Ga₃d core level binding energies for films deposited on semi-insulating GaAs(110) substrates under a range of temperatures.

Ga₃d binding energy associated with Ga₂O₃ oxide shows a correlation with deposition temperature. Increased temperature at the substrate would promote further
Figure 6.1: XPS depth profile of a $\text{Ga}_2\text{O}_3$ film deposited on GaAs(110)
6.2. XPS Oxide Analysis

oxidation of the gallium flux, via increased surface diffusion and kinetic energy, and reduced Ga:O ratio from Ga desorption. These values are in good agreement with reported values of Ga$_2$O$_3$ deposited by e-beam evaporation [76]. Substrate temperature in these experiments ranged from 360°C to 550°C, and a Ga3d binding energy shift of 2.0 ± 0.2 eV from Ga bonded to Arsenic was observed in this range. It is important to note that the e-beam deposition of Ga$_2$O$_3$ required additional oxygen introduced into the chamber to maintain ideal stoichiometry.

Incomplete oxidation of the gallium flux is observed by the lower energy peak, associated with suboxides of gallium. Energies similar to these are found on as-is substrates, where the known oxide is GaAsO$_4$. Peak energies of these suboxide binding energies increase with deposition temperature, which indicates an increase of the y:x ratio of this separate suboxide, Ga$_2$O$_y$. This is accompanied by a concomitant decrease in relative atomic percent, since more of the gallium is oxidized to the thermodynamically favored Ga$_2$O$_3$.

Oxide composition is dependent on initial substrate conditions – not only temperature, but doping type, and other impurities (for example, see [76]). Despite the values reported here, suboxide relative atomic percent was not consistent with deposition temperature for all the analyzed samples. It is possible that these peaks are simply fitting artifacts. GaO and Ga$_2$O are reported to be unstable and volatile[73]. Rutherford backscattering spectroscopy suggests that all the gallium is bonded as Ga$_2$O$_3$. There is no evidence of elemental gallium, which exhibits a peak between
6.3 Film Stoichiometry

Stoichiometry of the films were analyzed by Rutherford Backscattering Spectroscopy (RBS). Oxygen concentration in the film was first determined by nuclear resonance analysis of $^{16}\text{O}(d,p)^{17}\text{O}$ reaction and was calibrated against a Ta$_2$O$_5$ sample, that has a known oxygen concentration of $3.90 \times 10^{17}$ atoms/cm$^2$. Gallium concentration was then determined by RBS; backscattering was measured with He$^+$ ion incident angles of 45° and 5° to the plane of the surface (See Appendix A for spectra). Table 6.2 summarizes values obtained. The Ga$_2$O$_3$ for these samples were deposited under identical conditions, save growth temperature: both were cleaned with hydrogen ECR plasma for 1 hour at 200°C, and oxygen to gallium flux ratio was 35. Deposition time was 30 minutes, with 35 ± 5 W of microwave power to the oxygen plasma.

As expected, a reduction in the Ga:O ratio is observed with increasing deposition temperature. At room temperature growth, a sticking coefficient of 1 is expected.
Increasing substrate temperature reduces this sticking coefficient. To maintain ideal stoichiometry gallium beam pressure must be increased or oxygen decreased. The latter is not feasible since oxygen pressure cannot be reduced below 5×10⁻⁵ Torr – this is the threshold pressure for ECR plasma ignition. Gallium beam pressure can be increased, which increases the growth rate, but this favors increased roughness[77]. The pertinent issue is whether this excess oxygen affects the properties of the Ga₂O₃ films.

### 6.4 TOF SIMS Depth Profile

Purity of the films were evaluated by time-of-flight secondary ion mass spectroscopy depth profile. Carbon, which was detectable throughout the native oxide (25 counts), is undetectable in the deposited Ga₂O₃ oxide, giving a maximum possible concentration of 7×10¹⁵ cm⁻³[78]. This further supports the claim that a large proportion of the carbon at the interface was removed by hydrogen ECR plasma cleaning.
Figure 6.2: Time-of-flight SIMS depth profile of a Ga$_2$O$_3$-GaAs structure. Films of are very high purity.
6.5 AFM and SEM

Surface roughness of as deposited film are shown to be extremely smooth, as shown by atomic force microscopy (see Figures 6.36.4). Roughness of films increased as growth temperature decreased; RMS roughness of a thick 100 nm film grown at 400°C was only 5.4 Å, and increased to 6.9 Å with a growth temperature of 200°C. The standard deviation of roughness of 4 Å is comparable to Ga2O3 films deposited by e-beam evaporation (4 Å)[24], though their thickness measurements were performed by ellipsometry, across a 2” wafer, as compared to AFM across a 5 µm area.

Increased thickness uniformity is observed on films grown at 400°C; a trench and hump is observed at for the depositions at 200°C. These features are aligned in one direction, that is, height is uniform along this axis. At this growth temperature, minimal or no surface diffusion is possible, and due to the glancing angle of the gallium flux, three dimensional growth by sidewall sticking occurs. Further evidence of three dimensional growth mechanisms are observed by the ~100 nm islands observed at both deposition temperatures – the island height for the lower temperature growth is a few nanometers higher. Maximum height difference between minimum peak and maximum peak was 8.94 nm for the 200°C growth, and 7.86 nm for the 400°C growth.

Figure 6.5 shows a cross sectional SEM image of a sample passivated with Ga2O3 which was deposited at 400°C, showing a very uniform, smooth film. This cross section is at 45° to the surface plane, since the cleavage plane of a (110) wafer is (101). Therefore, the thickness of the Ga2O3 film measured from this picture is
Figure 6.3: Atomic Force Microscopy Image of Ga$_2$O$_3$ deposited on GaAs(110) @400°C. RMS Roughness is 5.4 Å

approximately 40 nm × cos 45° = 28 nm. Ga cell temperature for this growth was 750°C (ie., giving a partial pressure of 8.7×10$^{-6}$ Torr), and the deposition time was 40 mins. From this image, deposition rate is approximately 7 Å/min.
Figure 6.4: Atomic force microscopy image of a $\text{Ga}_2\text{O}_3$ film deposited at 200°C. RMS Roughness is 6.9 Å.
Figure 6.5: Cross sectional SEM image of a Ga$_2$O$_3$(dark) on GaAs
Chapter 7

Gallium Oxide Passivation: Optical Characterization

7.1 GaAs(110) undoped

7.1.1 Room Temperature Photoluminescence

Benefits of Ga$_2$O$_3$ passivation were realized by room temperature PL spectra on undoped GaAs(110) surfaces, showing an enhancement up to an order of magnitude increase (See Figure 7.1). Peak intensity was determined to be a function of substrate temperature and hydrogen plasma treatment conditions. Highest PL gain was obtained at a growth of temperature at 400°C, with only one hour of cleaning. Slightly less gain was attained by the 200°C growth, but hydrogen ECR cleaning was at a higher temperature, and for twice the time. The benefit of this lengthy, temperature
Figure 7.1: Room temperature PL spectra of GaAs(110) passivated with Ga$_2$O$_3$.

Aggressive cleaning is shown by the PL enhancement for this sample (0417110u) over 0402110u. The peak intensity doubles for 50% higher cleaning temperature and twice the hydrogen treatment time. Further evidence is shown by comparison of the two growths at 100°C (0430110u, 0425110u); the spectra for these samples suggest a greater dependence of cleaning on temperature rather than on cleaning time, since cleaning temperature was 50% greater and cleaning time was only 33%.

Peak energy shift from reference to passivated samples were very small. The
Legend of 295K PL Spectra for passivated GaAs(110)u

<table>
<thead>
<tr>
<th>Sample ID</th>
<th>H cleaning</th>
<th>Ga$_2$O$_3$ Deposition</th>
<th>Relative PL Enhancement</th>
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<td>u0404110</td>
<td>200 / 60</td>
<td>400 / 30</td>
<td>11.4</td>
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<td>u0417110</td>
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</tr>
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<td>u0430110</td>
<td>300 / 120</td>
<td>100 / 30</td>
<td>5.8</td>
</tr>
<tr>
<td>u0402110</td>
<td>200 / 60</td>
<td>200 / 20</td>
<td>3.5</td>
</tr>
<tr>
<td>u0425110</td>
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<td>100 / 20</td>
<td>2.5</td>
</tr>
<tr>
<td>Ref10u</td>
<td>none</td>
<td>none</td>
<td>1</td>
</tr>
</tbody>
</table>

Table 7.1: Processing conditions summary of GaAs(110)u passivated with Gallium Oxide

The largest shift was coincidentally observed by the sample with the largest PL enhancement from 870.7 nm to 872.7 nm, or 3.3 meV. Carbon manifests itself as an acceptor 26 meV above the valence band, and this peak shift to higher energy indicates that the predominant radiative recombination is shifting from conduction band to carbon acceptor, to conduction to valence band. Surface stress from the difference in thermal expansion coefficients is unlikely, since films are amorphous and in the nanometer thickness range.

### 7.1.2 5K Photoluminescence

Figure 7.2 shows low temperature photoluminescence spectra taken at 5K, with low excitation power of 2.5 mW. Midgap spectra at this temperature are compared for an unpassivated as is GaAs(110) wafer and sample 0402110u (See Table 7.1), with observed enhancement over the reference of 3.5 times at room temperature. There are three significant reductions in midgap peaks post passivation. Peaks at 0.75 eV
and 0.8 eV are known as the 0.80 eV PL band, and have been determined to correspond to the As\textsubscript{Ga} antisite defect\cite{35}. The most significant reduction comes from the 0.87 eV transition, which is attributed to oxygen on an arsenic site ($h\nu = \text{e-O}_\text{As}$)\cite{35} (Oxygen in an As site usually gives a photon at 0.635 eV; this was below the equipment’s detection range). In addition to the XPS interface profile, this gives further evidence that the oxygen at the interface is exclusively bound to gallium in the deposited oxide, and does not introduce deep donor levels. Given the relatively small room temperature PL increase for this sample, and the drastic reductions in these non-radiative recombination defect channels, it appears that further enhancement is limited by either residual carbon, or interface disorder due to low temperature deposition (according to the DIGS model), or by residual As\textsubscript{Ga} antisite defects (AUDM model).

Reduced optical activity of carbon is observed in low temperature PL spectra in Figure 7.3. Carbon is shown to significantly decrease in concentration at the surface from the SIMS data after hydrogen ECR treatment, but low temperature PL spectra indicates that carbon in the substrate is also passivated from this treatment\cite{79}. Transitions associated with carbon include Free-to-Carbon Acceptor (e-A\textsuperscript{o}) and donor-acceptor pair (D\textsuperscript{o}-A\textsuperscript{o}) transitions, having energies of 1.494 eV and 1.490 eV, respectively. Both peaks show a marked increase in luminescence intensity, indicating reduced acceptor activity (Pan et al.\cite{79} report that the D\textsuperscript{o}-A\textsuperscript{o} peak primarily increases after hydrogen treatment, however they used a lower excitation intensity of
Figure 7.2: 5K Photoluminescence spectra of unpassivated GaAs(110) and Ga$_2$O$_3$ passivated GaAs(110) (sample 0402110u)
2.5 mW/cm²). Post passivation spectra are narrower close to these transitions, indicating a reduction in carbon-related recombination causing non-homogenous broadening.

Additional evidence of reduced carbon activity is given by the appearance of a peak at 1.514 eV. The 1.514 eV peak is associated with ionized donor bound exciton \((D^0,X)_{n=1}[79]\) and/or neutral donor \((D^0,h)\) to valence band[35]. This peak is reported unobservable with as-is samples, since recombination in this spectral region is dominated by acceptor bound exciton \((A^0,X)\) due to the high concentration of carbon[79]. After hydrogenation, the authors report that the intensity of this peak is reduced and the \((D^0,X)_{n=1}\) transition dominates since a significant proportion of the carbon has been electrically deactivated. This phenomenon is observable in Figure 7.3, where post-passivation spectra shows the appearance of the \((D^0,X)_{n=1}\) peak at 1.514 eV.

The higher quality of the surface after passivation is inferred from the 5K PL spectra. The appearance of a double peak at 1.457 eV is also related to reduced carbon concentration, which is only observable after hydrogen treatment. This peak has been identified as the Longitudinal Optical (LO) phonon replica of the free-to-bound \((e-A^0)\) and donor-to-acceptor \((D^0-A^0)\) transition[80]. Additional evidence of surface enhancement is given by the removal of the broad shoulder of the \((D^0-A^0)\) peak – this shoulder originates from acoustic phonon coupling with the valence band through static lattice deformations, known as deformation and piezoelectric electron-
phonon interactions[81]. These deformations, for these samples, most likely originate from the high carbon concentration and/or \( \text{As}_{\text{Ga}} \) antisites and/or \( \text{As}_f \) interstitials. The fact that the shoulder width is considerably reduced, even with the \( \text{Ga}_2\text{O}_3 \) film, suggests that this film does not impart substantial stress, and that these impurities and defects are considerably reduced. Peaks in this spectral range can also be related to the \( \text{Ga}_{\text{As}} \) antisite defect[80][82][83], but the FWHM of the 1.457 eV peak reported here (8.7 meV), is narrower than that expected for \( \text{Ga}_{\text{As}} \) related transitions (25-50 meV[82]).

Hydrogen ECR plasma, in addition to reducing carbon electrical activity, has also been reported to slowly etch the GaAs substrate, inducing minor surface roughness[73] (for (100) surfaces; (110) surface are less reactive[2]). The removal of the oxide, which may induce minor surface roughness is the likely origin of the 1.358 eV peak. This peak is reported to be either the \( \text{As}_{\text{Ga}}\text{-Si}_{\text{As}} \) transition[84], \( \text{V}_{\text{As}}\text{-Si}_{\text{As}} \) transition[84], or the \( \text{V}_{\text{As}}\text{-Zn}_{\text{Ga}} \) transition[85]. The assignment of the latter two to the 1.358 eV peak is more reasonable, since the midgap spectra show a drastic decrease in transitions related to the \( \text{As}_{\text{Ga}} \) antisite double-donor. The reduction of these antisites and the native oxides at the surface by hydrogen ECR treatment may be the origin of As vacancies. This is plausible as observed from the 5K midgap spectra, where the major intensity reduction comes from oxygen in an As site. If the hydrogen plasma removes the \( \text{O}_{\text{As}} \) then the cleaned surface has an increased number \( \text{V}_{\text{As}} \). It appears at 200°C, that the Ga flux predominantly forms gallium oxide, rather than occupying
7.2. p-type GaAs(110) Passivation

Figure 7.3: LT-PL spectra of passivated and as-is GaAs(110).

the arsenic vacancies forming Ga₅₅ antisites.

7.2 p-type GaAs(110) Passivation

7.2.1 Room Temperature Photoluminescence

Heavily Zn-doped (10¹⁹ cm⁻³) GaAs(110) wafers were passivated under similar conditions to the undoped wafers. Figure 7.4 shows a room temperature-PL spectra similar to those for passivated undoped samples. Cleaning conditions and growth
Summary of 5K Photoluminescence Peaks for undoped GaAs (110)

<table>
<thead>
<tr>
<th>Energy (eV)</th>
<th>Transition</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.514</td>
<td>(D^0,X)_{n=1}</td>
<td>[79][35]</td>
</tr>
<tr>
<td>1.494</td>
<td>(e-A^0)</td>
<td>[79][35]</td>
</tr>
<tr>
<td>1.490</td>
<td>(D^0-A^0)</td>
<td>[79][35]</td>
</tr>
<tr>
<td>1.457</td>
<td>LO phonon replica of (e-A^0)</td>
<td>[80]</td>
</tr>
<tr>
<td>1.358</td>
<td>V_{As}-related</td>
<td>[84][85]</td>
</tr>
<tr>
<td>0.874</td>
<td>(e-O_{As})</td>
<td>[35]</td>
</tr>
<tr>
<td>0.8</td>
<td>As_{Ga}</td>
<td>[35]</td>
</tr>
<tr>
<td>0.75</td>
<td>As_{Ga}</td>
<td>[35]</td>
</tr>
</tbody>
</table>

Table 7.2: Summary of PL peak energies for GaAs(110) undoped
time were kept constant to show the effect of growth temperature on PL enhancement. As with undoped wafers, an increase in PL enhancement with increasing deposition temperature.

Samples 0123110pT and 0123110p are of same growth conditions, but the sample denoted with T had a thicker coverage. Since the gallium flux is the limiting factor for growth, the area of thin coverage denotes oxygen rich conditions, which may have led to arsenic oxide formation, explaining the reduced PL enhancement. This reasoning is supported by XPS Ga3d core level spectra, where Ga3d core level spectra associated with Ga_2O_3 bonding is higher by 0.03eV (21.20 vs. 21.23 eV) in the oxygen rich growth condition. Furthermore, suboxides detected in the range of 20 eV, reduce in concentration from 12.66 at% to 6.05 at%. Figure 7.5 shows monochromatic spectra (90° take-off angle) of Ga3d spectra of the deposited gallium oxide. Despite the larger atom fraction of Ga3d peak associated with Ga_2O_3 (85.41 vs. 78.05 at%) in
Figure 7.4: Room temperature photoluminescence spectra of passivated p type GaAs(110)

the oxygen rich growth condition, PL enhancement was lower, suggesting successful passivation is not governed by stoichiometry.

At 300K, and at this high doping level band-gap narrowing is observed. The high Zn doping creates a mini band that overlaps into the valence band; strong hole-hole interaction takes place between these levels. Further hole levels are contributed by carbon impurities, since it manifests itself 26 meV above the valence band. Charge balance at the surface is between Zn$_{As}$, C$_{As}$, and Ga$_{As}$ ionized acceptors, double donor As$_{Ga}$ antisite surface states, and free carriers. This can be represented by the charge
Table 7.3: Experimental conditions and room temperature photoluminescence data for passivation of p-type GaAs(110).

Figure 7.5: XPS Ga3d core level spectra for sample 0123110pT.
balance equation:

\[ n_o + n_1 + N_a^- + N_t^- + n_t = p_o + p_1 + N_d^+ + N_d^{2+} \]  

(7.1)

where the subscripts \( o, 1, \) and \( t \) represent equilibrium, excess, and trap carrier concentrations, respectively. \( N_a \) and \( N_d \) are acceptor and donor densities where \( p_o \) is comprised of Zn, C and valence band contributions. \( N_t \) would consist of Ga\(_{As}\) antisite. \( N_d \) consists of the double donor As\(_{Ga}\) antisite. All donors are ionized at room temperature, so the effects of passivation can be observed in room temperature PL spectra, since change in net acceptor concentration can be correlated to spectral halfwidth and peak position.

Figure 7.7 and 7.8 shows the relation of hole concentration and peak energy, where peak energy decreases with increasing hole concentration, at low and room temperatures, respectively. Table 7.3 lists the peak energies and the FWHM's of the passivated samples. The reference untreated sample has a large amount of As\(_{Ga}\) donors, which compensate the Zn acceptors; at the same time the high carbon concentration will interact with the valence band and Zn acceptors. Sample 0129110p shows a blueshift of the peak by 7 nm (11.25 meV) and spectral halfwidth reduction, indicating reduced net hole concentration. Increasing deposition temperature is accompanied by increased net hole concentration.

The peak energy shifts of the treated samples is dominated by shallow dopant neutralization by hydrogen incorporation. Wang et al.[86] report similar reduction
in net hole concentration, with penetration depth of up to 1 μm (30 min, 200°C, 4.8 mTorr). Greater dopant neutralization is expected with the higher Zn concentration, making hydrogen trapping more probable. Under photon irradiation from the ECR plasma, excess carriers can neutralize bound hydrogen to form hydrogen gas, by the following reaction[86]:

\[
(Zn_{Ga}H^+) + e^- \rightarrow Zn_{Ga}^- + H^o \rightarrow H_2
\] (7.2)

Increasing temperature will assist the formation and liberation of hydrogen, which explains the PL peak red-shift of the higher deposition temperatures. Without photon irradiation hydrogen liberation is significantly less: Pearton et al.[87] report that the fraction remaining of the initially neutralized donors after 400°C dark anneal is less than 40%, for p-type wafers (using deuterium, instead of hydrogen).

### 7.2.2 5K Photoluminescence

Low temperature photoluminescence spectra of sample 0123110p was compared to the untreated wafer. As with room temperature spectra, the predominant radiative transition is conduction band to acceptor (e, A). The peak is also referred to as $E_M$, where this peak is not associated with any direct transition, but merely the maximum luminescence[88]. Hole concentration of these substrates can be determined by peak PL position of 5K PL spectra, which can be calculated by the formula taken from[89]:

...
\[ E_p = 1.52 - 4.1 \times 10^{-6} \times p^{0.215} \]  

(7.3)

where \( E_p \) is peak energy and \( p \) is hole concentration. Figure 7.6 shows 5K PL spectra, with observed peak positions of 1.471 eV and 1.47 eV for passivated and unpassivated samples. Assuming photoluminescence uncertainty is less than \( \pm 0.001 \) eV, this gives hole concentrations of:

\[
E_p = 1.491 \text{ eV}, \quad p = 8.03 \times 10^{17} \text{ cm}^{-3}
\]

\[
E_p = 1.490 \text{ eV}, \quad p = 9.41 \times 10^{17} \text{ cm}^{-3}
\]

The lower value of hole concentration of the passivated sample agrees well with the observed reduced hole activity of the sample at room temperature.

The origin of the shoulder denoted in Figure 7.6 by 'S' is not positively identified at this time. It appears for doping concentrations greater than \( p>3.8 \times 10^{18} \text{ cm}^{-3} \) and a maximum at \( p=8 \times 10^{18} \text{ cm}^{-3} \) and attenuates at larger hole concentrations[18]. This peak appears at \( 1.485 \pm 0.005 \text{ eV} \)[90], which is below the intrinsic gap at 5K, 1.514 eV. This feature was initially explained as a K-nonconserving process[88], that is, indirect transitions or nonvertical transitions between the conduction band and the Fermi level below the top of the valence band. However it was argued that this cannot be the case, since this peak can be shifted to above-bandgap energies with high excitation power[90], and conclude that this transition may be a part of the \((e,
7.2. p-type GaAs(110) Passivation

Figure 7.6: LT PL spectra of passivated p type GaAs(110). 'S' denotes the shoulder found in highly doped p-type GaAs.

A) peak due to the transition from the conduction band to the bottom of the impurity band. Treatment by hydrogen and passivation by Ga$_2$O$_3$ did not show change in the behavior of this peak. Normalized spectra show no change in peak intensity ratio of the (e, A) transition to the S peak, nor changes in FWHM (fitted by gaussians).
Figure 7.7: PL Peak energy vs. hole concentration. Source: Hudait et al. 1998[18].

Figure 7.8: Room temperature PL peak energy vs. net hole concentration. Source: Ettenberg 1975[10]
7.3 n-type GaAs(110)

7.3.1 Room Temperature Photoluminescence

Low resistivity n+ contact layers are used to contact the active pn junction structure in GaAs-based laser diodes. Passivation of these layers is crucial for lowering the threshold current and the heat generated during operation. GaAs(110) wafers degenerately doped with silicon (n=1 \times 10^{18} \text{ cm}^{-3}), underwent passivation treatments. Silicon acts as a hydrogenic donor, having a Bohr radius of 100 Å in GaAs and manifests itself as a state 6 meV below the conduction band minimum. At low doping levels, interactions between the donor wavefunctions is minimal. At higher doping, as is the case with these substrates, there is strong interaction of the donor electron wavefunctions and this creates a mini band, and broadens with increasing doping concentration. At sufficiently high concentrations (>5 \times 10^{17} \text{ cm}^{-3})[91] this mini band overlaps into the conduction band. The PL spectral lineshape at this doping is symmetric, with peak energy shifting to higher energies as described by the Berstein-Moss effect, where the donor band overlap fills the conduction band. The predominant radiative transition then blueshifts, as calculated by a variant of the Bernstein-Moss equation relating peak energy to electron concentration[92]:

\[
E_{\text{max}} = 1.426 + 2.4 \times 10^{-14} \, n^{2/3} \, \text{eV}
\]  \hspace{1cm} (7.4)

Figure 7.9 shows 300K PL spectra of samples passivated with Ga_2O_3 deposited
## Experimental Summary of n-type GaAs(110) Passivation

<table>
<thead>
<tr>
<th>Sample ID</th>
<th>H cleaning</th>
<th>Deposition °C / min</th>
<th>Rel. Peak Intensity (a.u.)</th>
<th>Peak Energy (nm)</th>
<th>Calculated ( n ) ((10^{16}) cm(^{-3}))</th>
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<td>0</td>
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</tr>
<tr>
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<tr>
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</table>

Table 7.4: Experimental conditions of n type GaAs(110) cleaned with hydrogen ECR plasma and passivated with gallium oxide

at a range of deposition temperatures and hydrogen cleaning times. The effect of hydrogen ECR plasma cleaning on donor activity can be observed by the peakshift of this spectra. At higher temperatures and cleaning times, increased incorporation of hydrogen species is observed from the peak energy redshifts of samples 0416110 and 0424110, which were both cleaned for 90 minutes at 300°C. From the above equation, net electron concentration drops from \(8.52 \times 10^{16}\) cm\(^{-3}\) to below calculable levels. Samples with moderate cleaning times (0108110n and 0130110n) showed an increase in \(E_{\text{max}}\) to 1.432 eV, and calculated net electron concentration to \(1.25 \times 10^{17}\) cm\(^{-3}\).

Room temperature photoluminescence peak intensity is not the most discernible way to observe reduced surface recombination velocity at the surface. Largest PL enhancement was obtained with room temperature plasma cleaning and room temperature \(Ga_2O_3\) deposition, of two times intensity. Passivation by hydrogen ions is the most likely explanation since cleaning was performed at room temperature. Lu
Figure 7.9: Room temperature photoluminescence spectra of n-type GaAs(110) passivated with Ga$_2$O$_3$
et al. report reduced band bending with room temperature hydrogen ECR treatment of similarly doped wafers, which they attribute to hydrogen surface passivation[72]. Benefits of long cleaning time and higher growth temperatures as realized on undoped substrates were not observed for n-type wafers. In fact, a peak intensity degradation is observed for sample 0424110n, where deposition temperature was at 200°C. Under the aggressive cleaning regime (300°C, 90 mins), a PL enhancement was only observed for deposition at 300°C. For more moderate cleaning(200°C, 30-60 mins), PL enhancement was observed for depositions at 200°C and 400°C.

7.3.2 5K Photoluminescence

Low temperature photoluminescence spectrum of sample 0130110n (hydrogen cleaned and passivated at 200°C) was compared with an untreated sample. Figure 7.10 shows both spectra. More details of the effect of hydrogen ECR plasma treatment and Ga₂O₃ deposition on n-type wafers can be obtained from this spectra.

The large broad peaks are all associated with the gallium vacancy complex, VₓGa. These vacancies are present in undoped and p-type GaAs, but are only optically active under certain charge complexes[93]. These charge complexes are predominantly found in heavily doped n-type GaAs[93], and act to compensate the donors. The VₓGa can assume four charge states: V₃₋Ga, V₂₋Ga, V₋Ga, and V₀Ga[94], with each complex optically active at different wavelengths. The peak energies associated with each charge state are listed in table 7.5. Values reported here are in excellent agreement with previously
Table 7.5: Summary of peak energies of 5K PL spectra of n-type GaAs

<table>
<thead>
<tr>
<th>Transition</th>
<th>As is</th>
<th>Passivated</th>
<th>Previously Reported</th>
</tr>
</thead>
<tbody>
<tr>
<td>SiGa−V̄^Ga</td>
<td>1.15eV (24.1)</td>
<td>1.15eV (21.7)</td>
<td>1.14[95][94]</td>
</tr>
<tr>
<td>SiGa−V̄̅^Ga</td>
<td>unresolvable</td>
<td>1.2eV</td>
<td>1.19-1.22[94]</td>
</tr>
<tr>
<td>SiGa−V̄^Ga, SiGa−V̄̅^Ga</td>
<td>1.34 (20.8)</td>
<td>1.335 (33.6)</td>
<td>1.30-1.33, 1.34[94]</td>
</tr>
<tr>
<td>V̅^As−AsGa</td>
<td>1.36</td>
<td>unresolvable</td>
<td>1.36[84]</td>
</tr>
<tr>
<td>V̅̅^Ga−AsI</td>
<td>1.47 (14.6)</td>
<td>1.47 (21.6)</td>
<td>1.467[35]</td>
</tr>
<tr>
<td>e−A_C</td>
<td>1.49</td>
<td>unresolvable</td>
<td>1.491[84], 1.489[35]</td>
</tr>
<tr>
<td>SiGa−Si̅^As or V̄^Ga−V̄̅^Ga</td>
<td>0.96</td>
<td>0.96</td>
<td>1.01[84], 0.96[96]</td>
</tr>
</tbody>
</table>

Reduction of undesirable carbon and As_Ca antisite concentration are observed from changes in peak energy position from as-is to passivated. This is observed by the removal or reduction in peak intensity associated with their respective transitions. As with the undoped substrates, evidence of carbon removal is observed in this spectra. The double peak at high energy of the reference sample is the sum of two peaks. The higher energy peak, is attributable to transitions of donor or free electrons to the carbon acceptor band, (D−A_c)=1.491 eV or (e−A_c)=1.492 eV[35][84]. This peak reduces in intensity from reduced carbon, and simultaneously hidden by the intensity increase of the 1.47 eV peak. 5K PL spectra of the undoped wafers, and SIMS data support the argument that carbon concentration at the surface is indeed reduced. Another peak found in the as-is sample is the 1.36 eV peak, which is associated with the As_Ca−Si̅^As transition[84]. This lies within the V̅^Ga−peak (1.34 eV), but the difference in height of these peaks gives evidence of the As_Ca reduction. The
passivated peak is more symmetric, appearing to contain only one Gaussian, whereas the as-is peak is clearly the convolution of two peaks. The reduced contribution of the As_{Ga} gaussian explains the peak shift to lower energy, from 1.34 eV to 1.335 eV.

The change in peak intensities from as-is to passivated is attributed to hydrogen ECR plasma treatment of the surface. The most intense peak in the as-is sample is the triply ionized V^{3-}_{Ga}, which is expected due to the high doping of this substrate. After moderate hydrogen ECR plasma treatment, triply ionized vacancies are compensated by hydrogen incorporation. The passivated sample was cleaned with hydrogen ECR plasma at 200°C, for 60 minutes, with power of 35 W. Reduction in intensity of the V^{3-}_{Ga} peak is accompanied by a drastic increase in the V^{-}_{Ga}, V^{0}_{Ga} transitions, suggesting that most of the hydrogen incorporates itself as two per vacancy. The ‘shoulder’ of the 1.15 eV peak is due to the increase in the 1.20 eV V^{2-}_{Ga} transition, though this increase is not as drastic as the V^{-}_{Ga}, V^{0}_{Ga} (1.33 eV) transition increase.

For these hydrogenation conditions, it is expected that only the vacancies in the near-surface region will be affected. By reducing the concentration of the V^{3-}_{Ga}, less compensation of the Si_{Ga} donors is expected, and is corroborated by room temperature peak blueshift of this sample by 1.5 meV. Net donor concentration increased from \(8.5 \times 10^{16} \text{ cm}^{-3}\) to \(1.4 \times 10^{17} \text{ cm}^{-3}\) as calculated from room temperature peak energy position. However, peak redshift was observed for more aggressive hydrogen cleaning – cleaning conditions for this substrate was 300°C for 90 minutes. Effects of this hydrogenation was removed by deposition temperature of 400°C, where no peak shift
was observed (sample 0426110n).

The broad peak centered around 0.96 eV, undergoes negligible change, and its slight reduction in intensity is from the reduction of the 1.15 eV peak. This 0.96 eV has been reported as the transition from SiGa – SiAs, (silicon in a gallium site to a silicon in an arsenic site, respectively) by Harrison et al.[84]. However, Liang et al.[96] argue that if this indeed is the case, this radiative transition should emit at higher energy. Their reasoning is that SiGa and SiAs, manifest themselves at 5 meV, and 35 meV below and above the conduction and valance bands, respectively. Even with donor-band broadening by the high doping concentration, this transition does not equate to the difference in their energy levels in the band gap. They propose that the origin of this transition is from the donor-acceptor pair of VAs–VGa, since increasing [As]/[Ga] growth ratio reduces concentration of the VAs, for which they observed a drastic decrease in peak intensity. This theory is not supported by this data; peak intensity at 0.96 eV does not change, suggesting that the number of VAs–VGa transitions has remained constant. However the observed increases of the 1.34 eV and 1.467 eV peaks suggest that VGa has increased.
Figure 7.10: 5K Photoluminescence spectra of as-is n-type GaAs(110) and sample 0130110n (cleaned with hydrogen ECR plasma at 200°C for 60 mins with Ga₂O₃ deposited at 200°C)
Chapter 8

Further Discussion

8.1 AsGa Passivation

The AsGa antisite (and its complexes, known as the EL2 level) is the dominant deep defect level in undoped GaAs [97] and its compensation of carbon is responsible for the semi-insulating properties required in some device applications. However, for optoelectronic devices, these AsGa antisites are centers for non-radiative recombination and are not desirable. The concentration of this level is somewhat dependent on the crystal growth method: As-rich melt-grown GaAs has a higher concentration than MBE grown GaAs, and exposure to air will lead to a high concentration of AsGa defects in the near-surface region for either[8], causing Fermi-level pinning and band-bending.

Methods of controlling the optical and electrical activity of the AsGa antisite de-
fects involve optical, thermal, and hydrogen treatments. It was found that the electrical and optical activity of the EL2 level can be bleached by optical excitation at temperatures below 140K\(^{[98]}\), to a metastable state (EL2-M), but is thermally regenerated above 140K. Attempts of Rapid Thermal Annealing (RTA) at 550\(^{\circ}\)C-650\(^{\circ}\)C for up to two minutes resulted in an increase in EL2 level antisite defects\(^{[99]}\). The authors explain that the increase is the result of As\(_I\) diffusion (which is abundant in As-rich melt-grown GaAs) that annihilate V\(_{Ga}\), creating further As\(_{Ga}\) defects. The only successful reduction of As\(_{Ga}\) activity that was stable at room temperature was by hydrogen plasma treatment\(^{[100]}\). The authors report the concentration of electrically active EL2 to decrease by an order of magnitude, after hydrogen treatment at 300\(^{\circ}\)C for one hour.

It is interesting to note that the atomic configuration of the EL2 metastable state (EL2-M) closely resembles that of a hydrogen passivated As\(_{Ga}\) antisite. In the case of optical bleaching, it was determined by first-principal pseudopotential calculations that a photon energy of 1 eV is required to excite the electron from midgap state \(A_1\) to a level \(T_2\) above the conduction band\(^{[97]}\). Once the electron is in the \(T_2\) state, the system becomes unstable due to Jahn-Teller distortion\(^1\), and forces the As atom in the Ga site to displace 1.4 Å in the (111) direction. This forms a new defect, the gallium vacancy-ar senic interstitial (V\(_{Ga}\)As\(_I\)) pair (see Figure 8.1). This defect

\(^1\)This theory asserts that if a magnetic ion is at a crystal site of such high symmetry that its ground-state degeneracy is not the Kramers minimum, then it will be energetically favorable for the crystal to distort in such a way as to lower the symmetry enough to remove the degeneracy. Source: Ashcroft and Mermin, p. 659\(^{[101]}\)
manifests itself electrically as a filled acceptor state above the valence band. The $A_1$ state which was in midgap, raises in energy to above the conduction band minimum. In effect, the bond between the $As_{Ga}$ antisite and the $As_{As}$ breaks, and it is these antibonding electrons that contribute states to the midgap, which are now pushed out of midgap due to optical bleaching.

Hydrogen passivation of a EL2 defect ($As_{Ga}$) results in a similar atomic configuration. In the model by Bonapasta[20], two hydrogen atoms occupy themselves along the (111) axis (see Figure 8.2). The first hydrogen incorporates at the antibonding (AB) site near the $As_{Ga}$ atom, forming a strong bond, with bond energy of 3.5 eV, and pulling the $As_{Ga}$ away from the $As_{As}$ atom. The stretching of this $As_{Ga}$-$As_{As}$ bond weakens it and favors incorporation of a second hydrogen atom that saturates the dangling bond of the $As_{As}$ atom at the bond center (BC) site. This complex is referred to as $As_{Ga}$-$H^+_2$ complex. The resultant electronic structure is one that corresponds to the two H-As bonds, that is, two filled levels in the valence band. Incorporation of hydrogen in other sites vicinal to the $As_{Ga}$ were calculated to be metastable with respect to the EL2-$H^+_2$ configuration.

Evidence of hydrogen passivation of $As_{Ga}$ is observed in photoluminescence spectra of passivated undoped-GaAs. Midgap spectra (see Figure 7.2) show a significant decrease in $As_{Ga}$ related recombination centers (0.75 eV and 0.8 eV) with only one hour of hydrogen ECR treatment at 200°C. The reduction in activity of $As_{Ga}$ cannot be accounted for in any other way; processing temperature was too low to permit $As_I$...
diffusion of the metastable complex[99]. According to conventional theory the hydrogen plasma merely removes native oxides, carbon contaminants, elemental arsenic, and may etch away some of the surface[73]. Adopting this theory only, no change or a slight reduction in room temperature PL is expected for samples cleaned under more aggressive conditions. However samples treated by hydrogen ECR plasma at 300°C for two hours (0417110u and 0430110u) showed a more than double increase in peak intensity over samples cleaned for only one hour at 200°C (0402110u and 0425110u). Hydrogen passivation of the EL2 defect is clearly the benefactor.

As observed by the room temperature PL enhancement of sample 0404110u (11.4 x, which was hydrogen treated for 200°C for one hour) surface recombination velocity is not solely governed by the passivation of As,Ga antisites. Sample 0417110u showed
8.1. \textit{As}_{Ga} Passivation

Figure 8.2: (Left) Atomic structure of a \textit{As}_{Ga} antisite in GaAs and possible interstitial hydrogen sites. The most stable configuration is determined to be a hydrogen on the BC site and another on the AB site, resulting in an atomic structure shown on the right. Source: Bonapasta 1995[20].

A PL enhancement of $8.7 \times$, even though hydrogen treatment was twice as long and at 50\% higher temperature than sample \textit{0404110u}. The further PL enhancement is attributed to the higher deposition temperature (400\degree C versus 200\degree C). Depositions at higher temperatures produce smoother films, as observed by AFM, which would then support the Disorder Induced Gap States model. Further support of this is given by samples \textit{0402110u} and \textit{0425110u} where the latter was hydrogen treated for 30 minutes longer, but the lower deposition temperature of 100\degree C resulted in a 40\% lower luminescence efficiency than the sample with the Ga$_2$O$_3$ deposited at 200\degree C. Reduced band bending by increased \textit{As}_{Ga} compensation by \textit{Ga}_{As} creation (via the gallium flux occupying $V_{As}$) is a possibility at these higher deposition temperatures. This would give this process an advantage – in addition to passivating EL2 by hydrogen, the
residual $\text{As}_{\text{Ga}}$ can be compensated by $\text{Ga}_{\text{As}}$ promoting flatband structure. At 200°C gallium surface diffusion would be minimal, and the probability of $V_{\text{As}}$ occupation would be low. This is corroborated by low temperature PL spectra of the passivated undoped wafer, where no peaks related to $\text{Ga}_{\text{As}}$ are observed, which are expected in the range of 1.44 eV[80].

In the 5K photoluminescence spectra of the n-type samples, the large, unexpected increase of the $(\text{Si}_{\text{Ga}}, V_{\text{Ga}}^{-1,0})$ (1.36 eV and 1.47 eV) transitions cannot be exclusively be attributed to hydrogen passivation of the charged gallium vacancies ($V_{\text{Ga}}^{-3,-2}$). The reduction of the 1.15 eV $V_{\text{Ga}}^{-3}$ peak is not proportional to the increase of the $V_{\text{Ga}}^{-1,0}$ peaks. Diffusion is also ruled out since sample 0130110n was entirely processed at 200°C. The increase of these transitions is most likely from the increased concentration of $V_{\text{Ga}}$ via EL2-$H_2^*$ complex formation. In the case of optical bleaching below 140K, the $\text{As}_{\text{Ga}}$ atom displaces 1.4 Å in the $(111)$ direction[97] forming a $V_{\text{Ga}}\text{As}_I$ complex. For EL2-$H_2^*$ formation, the $\text{As}_{\text{Ga}}$ atom displaces 0.71 Å, past the barrier distance of 0.6 Å, adequate for EL2 passivation, and 5K photoluminescence also suggests that optically active $V_{\text{Ga}}$ is formed. From the spectra, the drastic increases in intensity arise from the $V_{\text{Ga}}^{-1,0}$ transitions (1.34 eV and 1.47 eV) of 61% and 48%, respectively. The $V_{\text{Ga}}^{-1}$ and $V_{\text{Ga}}^0$ charge states are energetically favored over $V_{\text{Ga}}^{-2}$[93], and since the EL2-$H_2^*$ complex already has a hydrogen on the $\text{As}_{\text{As}}$ dangling bond at the bridge-center site, the formation of $V_{\text{Ga}}^{-3}$ according to the EL2-$H_2^*$ model, is not favorable.
8.2 Hydrogen Passivation of Shallow Dopants

In addition to EL2 passivation, atomic hydrogen ECR plasma is also known to passivate shallow acceptors [86][102]; this may or may not be desirable. For optoelectronic devices, dopant passivation would be beneficial in the near surface region so as to hinder carrier migration to the surface. However, should the dopant passivation extend too far beyond the near-surface region, carrier delivery to the active layer is hindered that would result in a higher resistivity, and higher threshold current.

Dopant deactivation is observed in the room temperature spectra for p-type GaAs, where hydrogen ECR treatment at 200°C and subsequent room temperature gallium oxide deposition resulted in a peak blueshift, indicating reduced net hole concentration. Hydrogen incorporation into the lattice competes between passivation of As_{Ga} antisites and the passivation of shallow Zn and C acceptors. The pertinent issue is not so much as to what proportion these complexes are hydrogenated, but rather which is more stable at elevated temperatures, and under photon irradiation.

Room temperature PL spectra of the p-type GaAs samples support the theory that hydrogen passivation of EL2 defects is more stable than for shallow Zn acceptors. At room temperature deposition, a peak blueshift is observed, and with increasing deposition temperatures, a concomitant redshift occurs. This redshift indicates that acceptors are being reactivated, and that the EL2 donors are not. If the EL2-H_{2} complexes were less stable, then a further blueshift of the peak would be observed, from increased acceptor compensation. Though the calculated hole concentration of
the sample processed at 400°C is not restored to that of the untreated sample, this is most likely due to residual hydrogen still bound to acceptors. About 40% of the hydrogen was found to be remaining after a 1 min. anneal at 400°C[87]. EL2-H₂ was also demonstrated to be more stable than hydrogen-donor complexes in n-type GaAs, where annealing at 450°C completely restored the electrical activity of shallow centers, and only partially that of EL2[103].

Additional evidence of EL2 stability is given by the FWHM of the p-type room temperature PL spectra. The peak energy position of these samples indicates that hole concentration is less for the passivated sample than the untreated sample, and accordingly, the FWHM should be narrower[10]. However the spectra of these samples show that the FWHM of the p-type samples processed at 400°C is greater (70 meV versus 67.8 meV) as compared with the FWHM of the untreated sample. This can be explained from the calculations of Bonapasta[20]. In his model, the EL2-H₂ complex electronic state is pushed out of the gap into the valence band. This unexpected broadening then, is attributed to the increase in the EL2-H₂ complex concentration. Maximum broadening is observed for samples processed at 400°C, concomitant with maximum acceptor reactivation. Increased broadening is expected for a sample with more defect-type centers[90].

Hydrogen ECR plasma treatment parameters can explain the seemingly trendless dependence of passivation conditions on n-type room temperature PL intensity. The room temperature PL intensity enhancement is found to be less dependent on Ga₂O₃
8.2. Hydrogen Passivation of Shallow Dopants

deposition conditions than on hydrogen treatment time and temperature. The highest PL peak enhancement was from sample 1114110n, which was treated at room temperature. At this temperature and for n-type doping, hydrogen diffusion into the bulk would be minimal[102], the arsenic oxides would be removed[26], and AsGa antisites in the near surface region would be passivated. This treatment of the near surface region would lower surface recombination velocity from the passivated surface states, and is the reason for the doubling of the peak intensity. Increasing the treatment temperature to 200°C-300°C, and the treatment times from 30 minutes to 120 minutes resulted in peak intensities less than of sample 1114110n, of 1.56, 1.49, and eventually became lower than the reference (0.96 and 0.66). With increasing time and temperature, increasing dopant passivation and increasing penetration of the hydrogen atoms into the bulk occurs. Hydrogen penetration is in the order of microns at these conditions[87], much longer than the penetration depth of the excitation laser (~120 nm[104]), and minority carrier diffusion length in n-type GaAs (~0.5μm[105]). The creation of other deep levels in n-type GaAs by hydrogenation is not observed[106], ruling out this possibility. The reason for reduced PL intensity is due to the reduced carrier concentration, and increased band bending. Increased band bending is reported after hydrogen ECR plasma treatment at 350°C[26] for similarly doped samples. Band bending can be calculated with respect to surface acceptor and carrier concentration for n-type samples from the following formula at thermal equilibrium[3]:
where \( v_s \) is band bending in eV, \( e_a \) is electron charge, \( N_{sa} \) is surface acceptor concentration, \( \varepsilon_s \) is the static semiconductor dielectric constant, \( \varepsilon_o \) is vacuum permittivity, \( N_d \) is bulk donor concentration. Also, PL intensity decreases with decreasing carrier concentration in this doping regime[32](maximum PL intensity was observed with doping concentration of \( \sim 2 \times 10^{18} \text{ cm}^{-3} \)), and sample 0424110n has reduced carrier concentration from the observed peak redshift. However sample 0416110n exhibited a peak enhancement despite the peak redshift – this enhancement cannot be explained by the limited data.

A final point regarding the superiority of ECR plasma over other high-energy hydrogen plasma delivery methods, in addition to minimal bombardment-induced damage, is that the flux densities of ECR plasmas are higher[86]. This higher flux density allows for deeper penetration depth, and increased degree of reaction with defects and dopants towards the surface. This was demonstrated by hydrogenating p-type GaAs with rf and ECR plasmas, where the ECR plasma resulted in a acceptor deactivation greater than an order of magnitude[86]. If ECR plasma results in acceptor deactivation ten times that of rf-plasma, and if rf-plasma hydrogenation resulted in a reduction of EL2 concentration by an order of magnitude[100]^2, then it is reasonable to conjecture that ECR hydrogenation passivates more EL2 defects.

^2 Although these prior studies were performed using (100) wafers, hydrogenation is less a function of surface orientation than flux density, temperature, and doping concentration/type.
than rf-plasma, under similar processing conditions\(^3\).

### 8.3 Surface Recombination Velocity

Both undoped and p-type wafers exhibit a positive trend in PL intensity with respect to deposition temperature (see Figure 8.3). However n-type PL spectra shows a reverse correlation. These disparate trends can be partially explained by equation 2.10. Undoped wafers exhibit the greatest PL gain, since trap density is much greater than intrinsic carrier density, thus photoluminescence output would be more sensitive to changes in \(N_t\). Relative PL for n-type wafers would not be as sensitive to changes in trap density; the dominating terms are carrier concentration, which is very high, and minority carrier diffusion length, which is very low.

Relative values of surface recombination velocity can be calculated from the peak photoluminescence intensity values. Equation 2.12 will be used. Values used in the equation are as follows for p-type samples obtained from[10]:

\[
D = 50 \text{ cm sec}^{-1} \quad \text{(electron diffusion coefficient)} \quad (8.2)
\]

\[
L = 5 \mu m \quad \text{(minority carrier diffusion length)}
\]

\[
\tau_r = 10^{-7} \text{ sec (radiative lifetime)}[21]
\]

Excitation laser used was a Nd:YAG laser at 532 nm at 10 mW. Absorption

\(^3\)No Deep Level Transient Spectroscopy were performed on any of the samples.
Figure 8.3: Relative room temperature PL enhancement as a function of deposition temperature and wafer type. 'undoped 1' refers to samples cleaned under moderate conditions; 'undoped 2' refers to samples cleaned more aggressively, at higher temperatures and longer times.
8.3. Surface Recombination Velocity

Coefficient for GaAs at this wavelength is\[35\]

\[ \beta = 7.5 \times 10^4 \text{ cm}^{-1} \] (8.3)

with refractive index at this wavelength of \( n = 4.10 \)[35], and reflection coefficient of

\[ R = \frac{(n - 1)^2}{(n + 1)^2} = 0.37 \]

Minority carrier generation rate is calculated using the formula\[104\]:

\[ G_0 = \beta F \int_{z=0}^{z=d} \exp(-\beta z) dz = 2.38 \times 10^{18} \text{ electrons cm}^{-3} \text{ sec}^{-1} \] (8.5)

assuming 100% quantum efficiency, and taking the penetration depth (\( z \)) of the excitation laser to be \( d = 120 \text{ nm} \)[104]. \( F \) is normal incidence photon flux of the excitation laser, which is calculated to be approximately:

\[ F = 1.5 \text{ W/cm}^2 \times 532 \text{ nm} \times hc = 4.01 \times 10^{18} \text{ photons cm}^{-2} \text{ sec}^{-1} \]

Inserting the above values into 2.12,

\[ v_{surf} = -10.0 \left( \frac{3.1416F - 2.4987 \times 10^{17}}{3.1416F - 6.6632 \times 10^9} \right) \] (8.6)

where \( v_{surf} \) must be positive, and \{2.12 \times 10^9 < F < 7.95 \times 10^{16}\}. \( v_{surf} \rightarrow \infty \) as photon output becomes very low, and \( v_{surf} \rightarrow 0 \) where nearly all carriers created combine to emit a photon. A similar relation was determined for n-type wafers, taking \( D = 10 \text{ cm/sec} \) and \( L = 1 \mu \text{m} \). Figure 8.4 plots surface recombination velocity.
8.3. Surface Recombination Velocity

as a function of room temperature photoluminescence peak intensity in both minority carrier regimes. For undoped wafers, the n-type parameters were used to calculate $v_{surf}$ since holes are the limiting carrier.

More precise values of $v_{surf}$ cannot be calculated without further experiments involving photoluminescence under a large range of excitation intensities[107]. From the calculations of Adamowicz et al.[21], maximum of $v_{surf}$ at this excitation range (calculated by equation 8.5) is approximately $10^6$ cm/sec. Worst case scenario was assumed and this value was used for the untreated wafers irregardless of doping type. From the room temperature PL intensities, reductions in $v_{surf}$ were then calculated.

The maximum $v_{surf}$ reduction is from sample 0404110u, which has value of $8.66 \times 10^4$ cm/sec. This is about 15 times greater than $v_{surf}$ obtained by in situ e-beam deposition of Ga$_2$O$_3$ on GaAs(100) (~5000 cm/sec)[107], and about 80 times greater than an ideal MBE grown Al$_{0.45}$Ga$_{0.55}$As–GaAs interface. Keep in mind the following factors: intial surface was assumed to have $v_{surf}$ of $10^6$ cm/sec; the intial surface was exposed to atmosphere; the surface orientation is (110) and not (100); and the initial surface is a mechanically polished substrate. Of the previous reports of passivation of mechanically polished substrates, this treatment is thusfar superior. Olego et al.[52] estimate a reduction by an order of magnitude in $v_{surf}$; and Viktorovitch et al.[53] report a PL intensity increase of only four times. In fact, the PL enhancement of $11.4 \times$ reported here is comparable to the enhancement of the air-exposed undoped MBE surface passivated by e-beam Ga$_2$O$_3$ of $<13 \times[24]$, even
Figure 8.4: Surface recombination velocity is nearly proportional to photoluminescence output under these approximations. $v_{\text{surf}}(\text{max})$ of $10^6$ cm/sec was determined to the the approximate maximum for photon injection in the order of $10^{18}$ photons/cm$^2$sec [21].
8.3. Surface Recombination Velocity

<table>
<thead>
<tr>
<th>Sample ID</th>
<th>Relative PL Peak Intensity</th>
<th>Calculated $v_{surf}$ (cm/sec)</th>
</tr>
</thead>
<tbody>
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<tr>
<td>p-type</td>
<td></td>
<td></td>
</tr>
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<td>$1.78 \times 10^5$</td>
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</tr>
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<td>0425110</td>
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<td>$3.97 \times 10^5$</td>
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<tr>
<td>n-type</td>
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<td></td>
</tr>
<tr>
<td>1114110n</td>
<td>1.94</td>
<td>$5.12 \times 10^5$</td>
</tr>
<tr>
<td>0108110n</td>
<td>1.56</td>
<td>$6.38 \times 10^5$</td>
</tr>
<tr>
<td>0130110n</td>
<td>1.49</td>
<td>$6.68 \times 10^5$</td>
</tr>
<tr>
<td>0416110n</td>
<td>1.37</td>
<td>$7.60 \times 10^5$</td>
</tr>
<tr>
<td>0426110n</td>
<td>0.96</td>
<td>$1.04 \times 10^6$</td>
</tr>
<tr>
<td>0424110n</td>
<td>0.66</td>
<td>$1.52 \times 10^6$</td>
</tr>
</tbody>
</table>

Table 8.1: About an order of magnitude decrease in surface recombination velocity is calculated for the sample with the highest relative peak PL intensity.
8.4 Surface Orientation and Passivation

Comparing these results of GaAs(110) passivation to previously reported Ga$_2$O$_3$ of GaAs(100), and keeping in mind passivation reports mentioned in the literature review, a conjecture can be made that the effect of passivation is less a function of surface orientation than of surface defect density. The real question is then, which surface orientation or reconstruction is more prone to create defects when passivated? Reports have already demonstrated the benefit of As-rich c(4×4) over (2×4) reconstructions[14][15] when passivated by silicon or sulphur, since the latter reconstruction is believed to create arsenic vacancies at the passivation layer interface.

Evidence given by STS spectra that compares P$_2$S$_5$ wet-passivated GaAs (100) and (110) surfaces further support the dominance of defects over orientation: the authors report the I/V spectra to be identical for (100) and (110) p-type GaAs[108]; n-type GaAs(100) showed less favorable properties than its (110) counterpart, but they attribute this to the fact that the (100) surfaces were prepared by chemically etching, whereas the (110) were cleaved. When passivating high quality surfaces of either orientation, excellent properties are witnessed on both: Ga$_2$O$_3$ on pristine freshly-grown (100) MBE surfaces and in situ cleaved (110) surfaces both demonstrate excellent properties, that is, very low interface state density[46], and COD-less InGaAs laser
8.4. Surface Orientation and Passivation

diodes[70], respectively.

Unfortunately not all surfaces encountered are in situ MBE grown or in situ cleaved, and the question is less of the passivation dependence on surface orientation, but more so which passivation method is more amenable to less ordered surfaces? For these surfaces, ECR-MBE deposition of Ga$_2$O$_3$ may have an advantage over e-beam evaporated Ga$_2$O$_3$. The key difference of the ECR-MBE process to e-beam, is that the Ga and O species are delivered separately and may impinge on the surface before reacting to form Ga$_2$O$_3$. Herein lies the advantage: these atomic species may diffuse on the surface and interact with it. The Ga atoms may occupy V$_{Ga}$ or V$_{As}$ vacancies, restoring order or compensating surface charge, respectively. Oxygen atoms, on sputtered surfaces, are governed by bulk thermodynamics and preferential formation of gallium oxide compounds is preferred over arsenic oxides on GaAs(110)[109]. e-beam evaporation delivery of Ga$_2$O$_3$ molecules to the surface would not promote interaction with the surface. However this is speculative and additional studies would be required.
Chapter 9

Summary & Conclusions

9.1 Summary

Smooth, epitaxial, high purity, stoichiometric Ga$_2$O$_3$ films have been deposited on GaAs(110) surfaces cleaned by hydrogen ECR plasma have shown a reduction in surface recombination velocity for undoped, p-type and n-type wafers.

In addition to removing native oxides and carbon on the surface, hydrogen ECR plasma was shown to passivate EL2 defect centers and residual carbon. This passivated state is preserved by the Ga$_2$O$_3$ thin film overlayer that prevents arsenic oxide formation or interaction of contaminants with the surface.

Suboxides were detected in the films, and reduced in concentration with increasing substrate temperature, but no correlation was found with photoluminescence enhancement. In fact, suboxide concentration was inconsistent with any deposition
parameters.

For p-type wafers, hydrogen also passivated the Zn shallow acceptors, but these complexes were found to be less stable than EL2-H$_2^*$ complexes under photon irradiation (from the ECR plasma) at elevated temperatures.

Hydrogen, in addition to passivating EL2 defects and donors, altered the charge states of the gallium vacancies in Si-doped n-type GaAs. This reduced the donor compensation by a minor amount, but more aggressive hydrogen cleaning resulted in donor passivation. The donor compensation may also be in part due to $V_{Ga}$ creation via EL2-H$_2^*$ formation, analogous to optical bleaching of EL2 to EL2-M (at T<140 K) which displaces the As$_{Ga}$ to form $V_{Ga}As_I$.

Undoped wafers were most amenable to aggressive hydrogen cleaning, which was observed by photoluminescence spectra, and is expected from the equation for surface recombination velocity, since trap density is the dominating term.

Undoped and p-type wafers exhibited a positive trend of photoluminescence peak intensity with deposition temperature, creating smoother films, supporting the Disorder Induced Gap States model. For n-type wafers, PL increase was more dependent on hydrogen treatment conditions, where less treatment was more beneficial.

An advantage of using the ECR-MBE process for Ga$_2$O$_3$ deposition is that the gallium flux may create Ga$_{As}$ antisites on the surface, compensating As$_{Ga}$ antisites and thus reducing band bending at the surface.

The hydrogen cleaning step may not be necessary for in situ MBE surfaces and
in situ cleaved surfaces, since these surfaces are expected to have a much lower $A_{S Ga}$ concentration in the near surface region.

9.2 Conclusions

Properties of ex situ GaAs(110) surfaces have been enhanced by dry treatment in a UHV chamber. The combination of hydrogen ECR-plasma treatment followed by in situ deposition of $Ga_2O_3$ by the ECR-MBE process on GaAs(110) ex situ surfaces reduces surface recombination velocity by greater than an order of magnitude. The enhancement of the surface is due to several factors: damageless native oxide and organic contaminant removal by hydrogen ECR plasma, hydrogen passivation of EL2 defects, hydrogen passivation of carbon, and smooth, high-purity, thermodynamically stable $Ga_2O_3$ films that form a sharp GaAs(110)-$Ga_2O_3$ interface. These films do not introduce any states within the band-gap or cause any lattice distortions. Another significant advantage of using ECR plasma is the higher flux density – this may result in a larger proportion of passivated EL2 in the near-surface region as compared with rf-plasma.

9.3 Future Work

The work presented in this thesis raises additional questions that warrant further work into this area of study. A combination of both theoretical and experimental
9.3. Future Work

studies would elucidate and/or corroborate existing theories.

Further characterization studies would give more information on the properties of these interfaces. Characterization methods such as low temperature photoluminescence, capacitance-voltage measurements, surface photovoltage spectroscopy, would give information on recombination channels and surface state density in midgap, and trap level energies. Obtaining a interface state density profile of the forbidden gap would allow comparison to other passivation techniques, and would also facilitate calculation of surface recombination velocity.

Experimentally, passivation of in situ cleaved and freshly grown MBE surfaces would be of interest. These surfaces are of higher quality than mechanically polished substrates; they have reduced As$_{Ga}$ vacancies, and have less step edges. What would be the passivation effectiveness of ECR-MBE Ga$_2$O$_3$ on these surfaces? Would hydrogen ECR plasma treatment of these surfaces passivate residual As$_{Ga}$ defects?

Theoretically, ab initio calculations would give valuable information on the interaction Ga$_2$O$_3$ on GaAs(110).
Bibliography


Appendix A

Characterization Equipment Specifications

A.1 X-ray Photoelectron Spectroscopy

XPS spectra of the samples were obtained ex situ using an Al Kα X-ray source (15 kV, 25 mA) on a Leybold MAX 200 X-ray photoelectron spectrometer. Both non-monochromatic and monochromatic x-rays were used at a take-off angle of 90°. Spectra were taken using pass energy of 192 eV and 48 eV.

For the depth profiling, a fine sputter rate estimated to be in the order of 1 nm was obtained by using Ar⁺ gun, at 3.5 keV, 3 mA filament current, employing a 2 mm × 2 mm raster. Excitation spot size was 1 mm × 1 mm. All the depth profile spectra used a non-monochromatic source with a 90° take off angle.
A.2 Photoluminescence Spectra

Room temperature photoluminescence were performed on a Bio-Rad RPM2000 by Accent Optical Technologies. The excitation source was a Nd:YAG, and the 532 nm line at 10 mW excitation power was used.

Low temperature PL spectra was performed at 5K using the 632.8 nm line of a HeNe laser, at 2.5 mW excitation power.

A.3 Time of Flight Secondary Ion Mass Spectroscopy

These measurements were performed at Surface Science Western, at the University of Western Ontario by James Francis.

A.4 Atomic Force Microscopy

AFM images were obtained at the Department of Chemistry, on a NT-MDT's Solver P-47.

A.5 Rutherford Backscattering Spectroscopy

RBS was performed at Interface Science Western. The following spectra were obtained from two separate samples. Ga$_2$O$_3$ was deposited at 25°C, and 400°C for samples 0129110p, 0403110u, respectively.
A.5. Rutherford Backscattering Spectroscopy

Sample 0129110P (45 Degree Beam Incidence)

Sample 0129110P (45 Degree Beam Incidence)

Sample 0129110P (5 Degree Beam Incidence)
A.5. Rutherford Backscattering Spectroscopy

Sample 0403110U (45 Degree Beam Incidence)

Sample 0403110U (45 Degree Beam Incidence)

Sample 0403110U (5 Degree Beam Incidence)