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Photoluminescence Properties of Novel III-V Semiconductor Systems

Shumithira Gandan
Department of Physical Sciences, Munster Technological University, Cork, Ireland,
shumi.gandan@mycit.ie

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Applied Physics and Instrumentation

Photoluminescence Properties of Novel III-V Semiconductor Systems

Shumithira Gandan

Thesis submitted for the degree of
Doctor of Philosophy
Thesis Advisor: Dr. Tomasz J. Ochalski

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Declaration

This thesis is entirely the candidate's own work, except where specified otherwise.

This thesis has not been submitted for an award in any other institution.

Author's signature: ____

Shumithira Gandan

Supervisor's signature: _____

Tomasz J.Ochalski
Abstract

Perturbation of the inherent radiation equilibrium in solids by an external energy could engender an emission of the superfluous energy as electromagnetic radiation, or luminescence. Photoluminescence methods precipitate this disintegration of radiation equilibrium often by supplying the external energy as photons with energies higher than the bandgap energy of the solid. Since the excitation energy momentarily transforms the medium before luminescence is emitted, photoluminescence experiments are able to produce diverse and intricate spectroscopic data detailing the optical properties of the solid as a measure of this transformation.

The pliability of allowed electron states in semiconductors have instigated burgeoning research in the engineering of their bandgaps for a variety of applications. Owing primarily to its non-destructive nature and flexibility of bespoke experimental setups to meet specific constraints and objectives, photoluminescence spectroscopy is a universally adopted tool in the optical characterization of semiconductors.

In this dissertation, electron and hole dynamics describing the luminescence properties of three types of novel semiconductor systems are derived with laser spectroscopy experimental techniques. This includes stacked layers of Type-II GaSb/GaAs quantum rings, InGaAsN:H quantum dots and AlGaAsSb quaternary alloys. The quantum ring ensemble exhibited long radiative recombination times and significant blue shifts of peak position energies with increasing excitation powers, in addition to demonstrating quantum coherence with Aharonov-Bohm oscillations. Time-resolved photoluminescence enabled identification of shallow and deep localization centres present in the quantum dots, formed as a result of hydrogen irradiation and dilute nitride incorporation in the host lattice. Finally, the substantial effects of Sb in the indirect bandgap quaternary alloy which dominate its optical characteristics have also been determined with photoluminescence experiments.
To those who believed in me
Publications

Manuscripts

*Optical spectroscopy of p-GaAs nanopillars on Si for monolithic integrated light sources*
SPIE Digital Library, Quantum Dots and Nanostructures: Growth, Characterization, and Modelling XIV conference (March 2017)

*Stacked ensembles of Type-II quantum rings exhibit clear optical properties,*
(Manuscript in preparation)

*Carrier dynamics of InGaAsN:H/GaAs site-controlled quantum dots,* (Manuscript in preparation)

*Recombination processes in MBE-grown AlGaAsSb quaternary alloys,* (Manuscript in preparation)

Oral presentations

*Carrier dynamics of novel site-controlled InGaAsN:H/GaAs quantum dots for single photon sources* [Invited presentation]

SPIE, Photonics West Conference & Exhibition, San Francisco, California, (February 2019)

*Time evolution of lasing emission in Nanowires/Nanopillars grown on Si* [Invited presentation]

SPIE, Photonics West Conference & Exhibition, San Francisco, California, (February 2019)

*Carrier dynamics of InGaAsN:H/GaAs site-controlled quantum dots for single photon sources*

Photonics Ireland (September 2018)

*Emission dynamics in Nanowires/Nanopillars lasers grown on Si*

Photonics Ireland (September 2018)

*InGaAsN:H/GaAs site-controlled quantum dots for single photon sources*

PROMIS Photonics by the Lake Conference, Lancaster, UK (July 2018)

*One ring to rule them all, one ring to bind them*

Tyndall National Institute Internal Conference, Ireland (April 2018)

*Carrier dynamics of Type-II GaSb/GaAs quantum rings for solar cells*
Redshift of lasing modes in time-resolved spectra for GaAs-AlGaAs core-shell nanowires lasers on silicon

SPIE, Photonics West Conference & Exhibition, San Francisco, California (January 2018)

Single-mode lasing in InGaAs nanopillars on SOI

SPIE, Photonics West Conference & Exhibition, San Francisco, California (January 2018)

Optical spectroscopy of p-GaAs nanopillars on Si for monolithically integrated light sources

SPIE, Photonics West Conference & Exhibition, San Francisco, California (January 2017)

Optical characterization of natural and CVD diamonds and diamond nano-particles; emission dynamics studies

33rd International Conference on the Physics of Semiconductors, Beijing (2016)

Poster presentations

Effect of Gallium composition in AlGaAsSb alloys for APDs

19th International Conference on Molecular Beam Epitaxy, Montpellier (2016)

Optical properties of Type-II GaSb/GaAs quantum rings

Photonics Ireland (September 2018)

Redshift of lasing modes in Time-Resolved spectra for GaAs-AlGaAs core-shell nanowires lasers on silicon

Tyndall National Institute poster competition (December 2017)

Optical spectroscopy of p-GaAs nanopillars on Si for monolithic integrated light sources

Tyndall National Institute poster competition (July 2016)
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1.

Introduction

1.1 Background

The motion of electrons in matter is governed by electromagnetic radiation. In the event of a collapse in the thermodynamic equilibrium of electrons, the electromagnetic field permeating the system is transformed. As atomic interactions are primarily dictated by electrons, a plenitude of insight on condensed matter systems can be acquired by accessing the fundamental constituent of electromagnetic force, \textit{i.e} photons.

Although the average charge of the electromagnetic (photon) field in an atom without external excitation is zero, the instantaneous value is not, as it is dominated by a zero-point energy term even in the absence of photon occupation. As a consequence, random electromagnetic field (photon) states are spontaneously created (and annihilate) as a non-zero average intensity of the electric field ($<E^2>$) exists at the position of a bound electron (\textit{e.g.} in an atom or in a quantum dot).

Oscillations of the electromagnetic field provide the bound electron with ‘action’, compelling it to fall from higher to lower energy levels, emitting the excess energy as a photon in a process known as spontaneous emission\textsuperscript{1}. The quantization of these electromagnetic field oscillations (establishing the existence of the perpetual background radiation and generation of vacuum modes) was the hallmark of quantum field theory first described by Paul Dirac in 1927\textsuperscript{2}.

It would nevertheless be an arduous task to harness spontaneous emission for any practical purpose due to its volatility, necessitating methods of procuring photon emission in a somewhat controllable manner.
External perturbation of electromagnetic radiation equilibrium in solids can generate photons in a process known as stimulated emission. Such photons are a direct reflection of the predilection of electron occupancy in the solid, which is in turn determined by diverse factors including atomic structure and type of chemical bonding between atoms. The hybridization of atoms which lead to bifurcations in the molecular orbitals nonetheless provide an elemental way of classifying solids based on the ease of electron mobility between the valence band (bonding orbital) and the conduction band (anti-bonding orbital).

For electrons to develop a current that opposes their induced electric field (i.e., conduct electricity), individual electrons must make the transition from an energy eigenstate that is stationary in time to a superposition of initial and final energy levels (ground and excited states). If conduction bands with unfilled states are located arbitrarily near the valence bands, infinitesimally small amounts of energies would be required for this transfer, resulting in solid conductors or metals.

Semimetals are similar, except that the ‘overlap’ between the conduction and valence bands exist at a single point. The opposite is true in an insulator, where the energy gap between the conduction and filled valence bands is so vast that migration to the conduction band becomes impossible. Semiconductors are a subset of insulators, but with the distinct difference of electron conduction under specific conditions. Although unable to conduct electrons at 0K, an appreciable volume of electrons can be excited from filled valence bands to unfilled conduction bands at sufficient temperatures. This transition probability, $P$, of electron conduction in a semiconductor can be written,

$$P = e^{-\frac{\Delta E}{k_B T}}$$

where $k_B$ = Boltzmann constant, $T$ = temperature of the system and $\Delta E$ = energy gap.

The electrical conductivity of materials predicated on the energy requirement for electrons to bridge the gap between conduction and valence band states can be depicted through calculations of specific material bandstructures as shown in Figure 1.1.
Figure 1.1: Bandstructures of metal (copper), semimetal (silicene), semiconductor (germanium) and insulator (diamond) with increasing energy gap.
Mathematically, the transition probability can be expressed via the Fermi-Dirac distribution function. This involves determination of the Fermi level, which can be defined as the highest energy level with electron occupancy at 0K. The position of the Fermi level in a semiconductor strongly depends on the work required (energetically) to add an electron to the material in accordance with Pauli’s exclusion principle and is thus related to the density of electron or holes in the material.

In an intrinsic semiconductor, the Fermi level is located mid-bandgap as electrons and holes share equal probability of occupancy. As less work is required to add an electron in a p-type semiconductor due to the excess of holes, the Fermi level is lower in energy and situated closer to the valence band edge. This situation is reversed in an n-type semiconductor. The Fermi-Dirac temperature dependent probability distribution of electrons, \( f(E) \), at a particular energy, \( E \), at temperature, \( T \) is written,

\[
f(E) = \frac{1}{e^{(E-E_F)/kT} + 1}
\]

where \( E_F \) = Fermi level and \( k \) = Boltzmann constant

\[\text{Figure 1.2: Fermi function showing the temperature dependent probability distribution of electrons where } T_1<T_2<T_3.\text{ At } 0\text{K, the probability of an electron having an energy below the Fermi energy, } E_{F0}, \text{ is 1, while the probability of an electron having energy above } E_{F0} \text{ is 0.}\]
It should be noted that the preceding discussion on electric conduction is a classical description of an ideal semiconductor and partial conduction in a solid can also be induced by impurities, decoherence in the crystal etc. Correspondingly, the flexible engineering of semiconductor bandgaps can be chiefly attributed to the reciprocity between electrons in their conduction and valence band states Notwithstanding their overwhelming success in revolutionizing various aspects of modern technology, research for ever more complex semiconductor material systems for a burgeoning variety of applications is an ongoing endeavour.

The different atomic groups that form semiconductors lead to various crystalline structures based on the periodicity of atomic arrangement in the semiconductor lattice. Due to the translation symmetry of the lattice, properties of semiconductors are often described with regard to a single unit cell containing all characteristics of the repetitive lattice building blocks. In III-V semiconductors, atomic arrangement commonly follows a zinc-blende (diamond if elemental semiconductor) or wurtzite pattern.

As Bragg diffraction of waves justify much of semiconductor crystal analysis in reciprocal space, a Brillouin zone is constructed from the atomic arrangement of a particular semiconductor. The Brillouin zone is the reciprocal unit of the primitive unit cell in real space or Wigner-Seitz cell containing exactly one lattice point and incorporates coordinates that represent the translational symmetry of the lattice. Numerical computations usually exploit this symmetry even further with the irreducible Brillouin zone. The differences between zinc-blende and wurtzite atomic arrangements are shown in Figure 1.3 with their respective Brillouin zones depicted in Figure 1.4.
Figure 1.3: atomic arrangement of GaAs nanowires grown with different crystallographic structures: face centred cubic zinc-blende (left) and hexagonal wurtzite (right) \(^8\)

Figure 1.4: First Brillouin zones of the truncated octahedron in zinc-blende (left) and hexagonal prism (right) crystals \(^9\) with marked symmetry points and lines.
The probability density of the electron wavefunctions at the symmetry points can then be computed using Schrödinger’s equation, with solutions in Bloch form. The allowed energy eigenstates are substantially influenced by the shape of the periodic potential, which depends on various factors such as the crystallographic and collective orbital structure of the atoms within the lattice. If this calculation is extended for many points within the Brillouin zone (often in the direction of the points of symmetry), a bandstructure is formed yielding the allowed electron energy levels within the semiconductor and the energies between them. The bandstructure of GaAs is shown in Figure 1.5.

![Figure 1.5: Bandstructure of GaAs plotted along symmetry points in a) Calculated band structure of GaAs using the tight binding method. b) Sketch of GaAs band structure near the Γ-symmetry point showing conduction band, heavy hole band (hh), light hole band (lh), and split-off band (so) in the X [100] and L [111] directions](image)

Considering that Heisenberg’s uncertainty principle limits their resolution, bandstructure plots typically assume infinite crystal periodicity. Although valid at large length scales and only within the lattice boundaries, bandstructures are essential to theoretically ascertain optical transition energies in a semiconductor crystalline structure.

The energy gap that electrons must contend with to conduct electric flow is labelled in Figure 1.5 as \( E_g \). In GaAs, the valence band maximum, \( E_V \) lies directly below the conduction band minimum, \( E_C \) but this is not necessarily the case. If the positions of...
$E_V$ and $E_C$ were varied in momentum, an additional momentum-matched particle, such as a phonon is imperative to promote electron transitions between the conduction and valence bands. This ‘direct’ or ‘indirect’ transition of electrons is portrayed in Figure 1.6.

![Figure 1.6: (Left)Direct and (right)indirect recombination transitions in a semiconductor. In indirect transitions, the excited electron can recombine with any hole as long as it is momentum matched with a suitable phonon](image)

In low-dimensional semiconductors, the types of materials that form the heterojunction can drastically alter the nature of electron transitions in the bandstructure; the dissimilarity is illustrated below in Figure 1.7. The band alignment in Type-I heterostructures enable direct confinement and recombination of the electron and hole quasiparticles. These heterostructures mimic the conduction and valence band transitions of direct gap bulk semiconductors and are employed in systems that require a substantial overlap between the electron and hole wavefunctions such as InAs/InGaAs/GaAs quantum dots-in-a-well\textsuperscript{11} and GaAs/AlGaAs/GaAs nanowire\textsuperscript{12} photodetectors, InGaAs/GaAs quantum dots for emission at the telecom O-band\textsuperscript{13} etc.

Engineering of the various band parameters in a heterojunction also enable semiconductor materials to create confinement for one type of carrier, while acting as an energetic barrier for the other species. This creates Type-II or Type-III semiconductor structures with reduced electron and hole wavefunction overlaps. The ensuing prolonged radiative recombination times in staggered gap Type-II systems have been utilised in
GaSb/GaAs quantum rings\textsuperscript{14} and CdS/CdTe heterodimers\textsuperscript{15} for solar cells, CuSbSe\textsubscript{2}/TiO\textsubscript{2} nano-photocatalysts\textsuperscript{16} etc. In Type-III systems, the maximum bandgap barriers result in a broken gap. Such structures could minimize tunnelling current in electronic devices and have been incorporated into BP/ReS\textsubscript{2} tunnel diodes\textsuperscript{17}, CdO/Si PMOSFET\textsubscript{s}\textsuperscript{18}, PtS\textsubscript{2}/WSe\textsubscript{2} high speed photodetectors\textsuperscript{19} etc.

\hspace{1cm} \includegraphics[width=1\textwidth]{Figure1.7.png}

Figure 1.7: Schematic of various band alignments in semiconductors with red arrows representing possible optical transitions. Barriers in materials of Type-II and Type-III materials can be engineered to reverse the confinement of either electrons (solid circles) or holes (empty circles)

The decay of electrons to their initial energy levels (ground state) in the instant after excitation, \textit{i.e} recombination, release photons that are collectively termed luminescence. Annihilation of the excited electron with its charge counterpart would then equal the lowest possible state of electron occupancy in the semiconductor, which is practically the energy gap. It is noted here that the charge counterpart of electrons, \textit{i.e} holes, are an arbitrary concept which do not exist in isolation and are not particles according to the standard definition. Their charge and mass properties are nevertheless akin to fermions\textsuperscript{20}, and for the purposes of the work in this thesis, they will be treated as particles.

The states that arbitrate luminescence in the semiconductor can be identified as possible radiative recombination channels. Here, the term ‘radiative’ directly implies that the emission is in the form of measurable luminescence. In two-level systems, the radiative transition rate follows the Fermi Golden Rule devised by Dirac.
The transition probability, $\lambda_{if}$ is defined as:

$$\lambda_{if} = \frac{2\pi}{\hbar} |M_{if}|^2 \rho_f$$

where $\rho_f = \text{density of final states}$ and (in the dipole approximation),

$$M_{if} = \int \Psi_f^* V \Psi_i \, dV$$

where $\Psi_f^* = \text{the complex conjugate of the wavefunction of the final state}$, $\Psi_i = \text{wavefunction of the initial state}$ and $V = \text{an operator denoting the physical interaction coupling the initial and final states of the system}$, also known as the matrix element

The mean lifetime of atomic transitions, $\tau$ is related to the Rule through,

$$\lambda_{if} = \frac{1}{\tau}$$

However, this relation is more complicated for semiconductors as parameters of the particular band structure come into play. The transition probability in a semiconductor system is contingent on diverse criteria such as\textsuperscript{21}:

- Joint density of electron and hole states available for participation in the recombination process
- Probability for suitable configuration of occupancy in the conduction and valence band states
- Quantum mechanical probability of the transition $|M_{if}|^2$ which is dependent on any number of factors affecting the wavefunction overlap between the initial and final states and provides a good approximation over a wide range of wavevectors close to the band extrema

Despite the complexity in exact determination of radiative transition probability, characteristics of electron distribution in a semiconductor ground state can be obtained in a ‘bottom-up approach’ by delineating the dynamics of electron-hole recombination.
1.2 Recombination dynamics in semiconductors

The optical transitions of an inchoate semiconductor system that are determined through experiments to garner luminescence ultimately lead to a derivation of its physical properties. In order to invoke luminescence, the external incident energy directed to a semiconductor can be applied in distinct forms (e.g. thermal energy, ultrasound vibrations, mechanical deformation etc). In the following discussion however, only recombination dynamics by photon excitation will be considered.

Under weak excitation, neglecting luminescence from electron-hole liquid, electron-hole plasma and Bose-Einstein type states, radiative recombination of electron-hole pairs can be categorised into:

1. donor–acceptor pairs (D\textsuperscript{0}-A\textsuperscript{0})
2. free hole with a neutral donor (h-D\textsuperscript{0}) or ionized donor (h-D\textsuperscript{+}) and a free electron with a neutral acceptor (e-A\textsuperscript{0}) or ionized acceptor (e-A\textsuperscript{+})
3. free electron–hole pairs (e-h) or band-to-band recombination

Recombination of free electron-hole pairs (e-h) involve direct band-to-band recombination unmediated by supplementary ground state levels. This type of recombination cannot occur if dopants, impurities or defects that affect the translational symmetry of the crystal are present in the lattice.

If an impurity has smaller (larger) valence electrons than the main constituents of the crystal lattice, it creates a shallow acceptor (donor) level in the bandstructure.

Radiative recombination can then transpire between free holes and neutral or ionized donors (h-D\textsuperscript{0}, h-D\textsuperscript{+}) or free electrons and neutral or ionized acceptors (e-A\textsuperscript{0}, e-A\textsuperscript{+}). The activation energies $E_A$ ($E_D$) thus correspond to the ionisation energy of acceptors (donor). Note that impurities can also encompass intentionally doped atoms in a semiconductor to increase electrical conductivity, produce luminescence at a specific wavelength etc.

A band diagram illustrating this process is shown in Figure 1.8. As an alternative to the bandstructure plot in Figure 1.5, a band diagram is plotted with the $x$-axis detailing direction of growth instead of momentum (Figures 1.8 and 1.9). These diagrams show
transitions in real space across a heterojunction, and often include features such as the bending of bands at interfaces, albeit at a macroscopic level.

Donor-acceptor pairs (D⁰–A⁰) radiatively recombine directly without mediation from free particles as shown in Figure 1.9. In this case, the neutral acceptor orbits the hole while the neutral donor analogously orbits the electron. A photon is subsequently released when the carriers annihilate. Although both the donor and acceptor become ionized immediately after recombining, free electron-hole pairs generated by the excitation quickly neutralise them before the process repeats.

This generic representation of radiative recombination in classic semiconductors can also be extended to acceptor-like or donor-like states in complex semiconductor
systems. For instance, an acceptor-like state could be formed by localized defect states in a nanostructure ensemble with Type-II band alignment seen in quantum rings discussed in Chapter 3. The complex growth dynamics of quaternary alloys could also bring about donor-like states in the conduction band of indirect AlGaAsSb alloy as addressed in Chapter 5.

Donor-like states have also been identified in ensembles of dilute nitride InGaAsN:H quantum dots in Chapter 4. Here, the incorporation of 2% nitrogen concentrations in conjunction with hydrogen irradiation create shallow and deep donor-like states all along the conduction band minimum.

In addition to the radiative transitions discussed above, the interaction of the atomic nuclei themselves with the surrounding crystal lattice cannot be neglected. As the absorption of a photon occurs too fast \((10^{15} \text{s}^{-1})\) for atoms in the semiconductor to change positions, lattice vibrations that are much slower \((10^{12}-10^{13} \text{s}^{-1})\) around the localized centre must rearrange into new equilibrium.

Whenever an electron returns to its ground state after excitation, oscillations are propagated to the surrounding lattice. The quanta of these vibrations are termed phonons and the magnitude of their interaction with luminescence phenomena is determined by the electron-phonon or exciton-phonon coupling coefficients. The non-radiative transitions as a result of phonon participation can transform the excitation energy into heat, new point defects in the lattice or result in photochemical changes in the material. When excitation energy is transformed into heat through multiphonon recombination, interaction of a localized centre within the lattice is necessary as the non-radiative analogy of bimolecular recombination is highly improbable from the perspective of perturbation theory.

This interaction will be considered within the framework of the configurational-coordinate (CC) model which expresses the total defect energy as a function of generalized coordinates\(^{22}\). The \(x\)-axis is therefore an overall measure of the atomic or ionic displacements of the defect atom, while the \(y\)-axis axis represents potential energy. Here, only the immediate environment of the defect atom is examined and the atomic nuclei of the impurity is assumed to be at rest during optical excitation (Franck-Condon
principle). However, it should be noted that the energy states belong to the entire crystal in reality, as a result of the electron wavefunction spreading in momentum space.

Figure 1.10: Multiphonon recombination. Energy transitions follow A-B-C-D

In Figure 1.10 above, g represents an excited state of a localized luminescence centre h within the bandgap, so that $Q_{h0}$ and $Q_{g0}$ are the lowest energy points of each parabola and $X$ is the point of intersection between the two vibrational modes. As point B is a non-equilibrium position, when a photon with an energy $h\nu_{B-A}$ is absorbed, the system gradually reaches point C, the local minimum of the parabola of the excited vibrational state. This excess energy $E_R$, or relaxation energy is released in the form of phonons to the lattice. The verticality of the A-B transition is determined by the excited electronic state with the highest probability of occurrence. Following this, the system not having attained equilibrium, releases a photon $h\nu_{C-D}$ as luminescence ($E_R$ is equal in both cases as the energy lost in B-C determines the energy left for C-D).

The relaxation energy $E_R$ can be defined as $S\hbar\omega$, where $S$ is a dimensionless parameter characterising the strength of the electron-phonon coupling known as the Huang-Rhys factor and $\hbar\omega$ is a single unit of lattice vibrational frequency indicated in Figure 1.10. Further, the impurity in question is strongly interacting with the lattice as exhibited by the large difference between local coordinates $Q_{g0}$ and $Q_{h0}$.
From the energies labelled in the figure, the energy difference $E_A$ from the intersection of both parabolic curves can be acquired. This is minimum energy required to ionise a particular defect and is calculated as,

$$E_A = \frac{(E_0 - E_R)^2}{4E_R}$$

In Figure 1.11, the cooling transitions for a localized centre is extended to include mediation from a deep level defect. The decay of the excited state $g$ of the localized centre $i$, is now impeded by a deep level $h$ which lies in the middle of the bandgap.

A defect associated with a deep level is always in strong interaction with the surrounding lattice and the configurational coordinate changes from $Q_{g0}$ to $Q_{h0}$ as the excitation energy gradually dissipates via $A$-$B$-$C$-$D$, with the final luminescence released as $h_{\text{C-D}}$. From Figure 1.11, it becomes readily apparent that an existing defect which is in weak interaction with the lattice ($Q_{g0} \approx Q_{i0}$), is indispensably encouraged by the presence of a deep level defect to participate in non-radiative recombination through multiphonon recombination. Non-radiative transitions facilitated by a deep-level defect such as this is often called Shockley-Read Hall recombination.

*Figure 1.11: Multiphonon recombination involving a deep level defect*
The volume and type of defects or impurities in a semiconductor system are dependent on factors such as growth parameters, alloy compositions, gradients in the interface of a heterojunction, surface recombination, strain in low-dimensional nanostructures, material fluctuations in the alloy etc. Although a completely pristine crystalline structure will not conduct any electricity, unintended defects beyond a certain threshold are detrimental to the radiative efficiency of a semiconductor. Some general categories of localized defects are shown in Figure 1.12 below.

![Figure 1.12: Common types of defects in semiconductors](image)

Apart from localized point defects, another non-radiative recombination mechanism for transforming excitation energy into phonons is Auger recombination. In this case, the excitation energy applied to the semiconductor is transferred to kinetic energy sufficient to dislocate another electron or hole which now act as the ‘impurity’. These hot particles then rapidly dispense their excess energy via phonons in the crystal matrix through quasi-continuum states. Auger processes dominate non-radiative phenomena when high carrier densities are involved especially in semiconductors with small volumes and those with relatively narrow bandgaps.
The three particles required for the non-radiative Auger process are either two electrons and a hole \((eeh)\) or one electron and two holes \((ehh)\). Possible types of Auger recombination processes are detailed in Figure 1.13\textsuperscript{24}.

![Diagram showing types of Auger recombination mechanisms. C- conduction band, S- spin splitoff band, H – heavy hole, L – light hole. 1 and 2 refer to order of transition between electrons (solid blue circles) and holes (empty blue circles) transitions are heavily dependent on the effective mass of each band.]

Figure 1.13: Types of Auger recombination mechanisms. C- conduction band, S- spin splitoff band, H – heavy hole, L – light hole. 1 and 2 refer to order of transition between electrons (solid blue circles) and holes (empty blue circles) transitions are heavily dependent on the effective mass of each band.

Considering that non-radiative processes occur in tandem with radiative recombination in a semiconductor system, the defect activation energy is an important parameter often discerned from photoluminescence experiments. Subsequently, the activation energy of localized defect states within the GaSb/GaAs quantum ring ensemble and its wetting layer are discovered in Chapter 3, in addition to Arrhenius plot calculations for the quantum rings and InGaAsN:H quantum dot ensemble in Chapter 4.
Based on the preceding discussion, the motivation for photoluminescence (PL) spectroscopy can be clarified. Firstly, the emission and absorption spectra which relate directly to the ground state recombination dynamics in the material system can be obtained. This allows perception of the mechanisms underlying thermal quenching of luminescence, effect of increased free carrier density, carrier cascade in complex multi energy-level systems, strength of electron-phonon coupling, identification of physical and chemical modifications to alloy composition and growth procedures etc.

The recombination dynamics in the material can also be quantified further by measuring decay transients. Employing time-resolved PL (TRPL) techniques, the exact time taken for the annihilation of the electron-hole pair after excitation indicating the length of radiative recombination pathways is determined. The carrier dynamics in the system then enables tracing of patterns related to the formation of semiconductor structures, identification of bandstructure valleys that contribute to luminescence, assessment of the quality of crystalline formation etc.

This thesis will focus on the photoluminescence spectroscopy experimental results of novel III-V semiconductor systems with PL and TRPL techniques. Depending on the investigated structure, physical parameters (temperature, excitation power, etc) are utilised to perturb the electromagnetic radiation equilibrium so that radiative and non-radiative recombination dynamics can be ascertained.

The emission dynamics are then delineated with respect to the physics of growth of the particular structure in order to determine, for example:

- recombination in stacked layers of GaSb/GaAs quantum rings which are heavily influenced by structural morphology such as their annularity and Type-II bandstructure
- influence of hydrogenation and dilute nitride on InGaAsN:H quantum dots and
- luminescence from the indirect bandgap of Al_{0.85}Ga_{0.15}As_{0.56}Sb_{0.44} quaternary alloy
1.3 Marie-Sklodowska Curie ITN Postgraduate Research on Dilute Metamorphic Nanostructures and Metamaterials in Semiconductor Photonics (PROMIS)

All three semiconductor structures investigated in this thesis were provided by academic partners within the Marie Skłodowska-Curie PROMIS consortium. This Initial Training Network (ITN) consisting of academic and industry partnerships is centred on developing core skills in novel semiconductors for specific applications in communications, security, energy and environment. Each structure was produced with initial target applications in:

- **Energy**
  GaSb/GaAs quantum rings were grown by Molecular Beam Epitaxy (MBE) in Lancaster University, UK as an intermediate band to increase the long wavelength absorption for increased efficiency intermediate band solar cells. In Chapter 3, stacked layers of GaSb/GaAs quantum rings are characterized optically.

- **Communications**
  InGaAsN:H quantum dots for single photon emitters at the low-loss telecommunication window were fabricated in a collaboration between two PROMIS partners. The InGaAsN quantum well was grown by Molecular Chemical Vapor Deposition (MOCVD) in University of Marburg, Germany and hydrogenated in Sapienza University, Rome. In Chapter 4, the carrier dynamics of 600nm quantum dot ensembles are established.

- **Security**
  AlGaAsSb alloys for an ultra-thin gain region in Avalanche Photodiodes (APD) were grown by MBE in Sheffield University, UK. In Chapter 5, the emission dynamics of indirect bandgap of Al$_{0.85}$Ga$_{0.15}$As$_{0.56}$Sb$_{0.44}$ is substantiated with experiment results.
1.4 Thesis outline

This dissertation will be presented in the following format. In Chapter 2, the laboratory instrumentation and experimental techniques for the acquisition of PL and TRPL data is described. Carrier dynamics from PL and TRPL experiments for the semiconductor structures outlined in Section 1.3 i) GaSb/GaAs quantum rings, ii) InGaAsN:H quantum dots and iii) Al_{0.85}Ga_{0.15}As_{0.56}Sb_{0.44} alloy will be discussed in Chapter 3, Chapter 4 and Chapter 5 respectively. Chapter 6 contains concluding remarks and main findings from the conducted experiments and suggestions for future work.
2. Experimental techniques

2.1 PL excitation and signal detection

Photoluminescence in semiconductors is customarily induced with a laser. Due to the limited photon energy dispersion in a laser output, the thermalisation of carriers can be traced to a single excitation energy, minimising the activation of non-radiative recombination centres and spurious spectral features. The coherent nature of lasers also facilitates polarisation sensitive PL measurements, and their constricted beam divergence permits precision in focus through free space optics or with an optical fibre.

Lasers with continuous wave (CW) outputs are pumped without interruption and are thus able to generate a steady output signal, with effectively equal average and peak powers. For this reason, they are ideally used in steady-state PL experiments. In a pulsed laser, the peak output power is generally substantially higher than the average output power. Figure 2.1 shows an example of average and peak output powers of a continuous wave and mode-locked pulsed laser with a repetition frequency of 80MHz.

Although both lasers have an average power of 10W, the pulsed laser has a peak power of 2.5kW. The high energies of 125nJ that are consequently contained in short pulse widths of 60ps will then enable excitation and measurement of fast carrier lifetimes largely limited by the width of the pulse.
It is also possible to adopt a pulsed laser for PL experiments if the rate at which available states in the semiconductor are filled by free carriers is orders of magnitudes longer than the laser pulse repetition rate. For example, an 80MHz pulsed laser can be used to measure PL in a sample with carrier lifetimes of 100ns. However, CW excitation might still be necessary if exact calculations and fitting of PL spectra peaks are required.

In Figure 2.2 below for instance, the carrier lifetime of the GaSb/GaAs quantum ring ensemble is 80ns at 8K and power-dependence PL experiments were done employing laser pulses with a 75.6MHz repetition (12.5ns period). Although a clear blue shift can be observed toward higher energies with the pulsed laser with high peak powers, accurate fitting with the power law and derivation of relevant physics could only be done with a CW laser.

The geometry of laser excitation is another essential factor for consideration in a PL setup. Two different configurations are used for PL excitation in this thesis, confocal and side reflection. When the plane of excitation and emission is the same, the setup is relatively easier to build as a single lens suffices for optimisation of alignment. The perpendicular arrangement of optical elements also minimises complication in positioning.
Figure 2.2: Excitation power dependence data of Type-II quantum rings with CW (discussed in Chapter 3) and 75.6MHz pulsed laser excitation

However, despite the long pass filters that are habitually placed before the monochromator entrance slit for signal dispersion (Appendix A3), strong laser intensities which are close to the emission energetically do unavoidably ‘bleed’ into the PL spectra since the laser excitation is focused alongside the collected emission. This could lead to a distortion of the spectra which prove pronounced especially if the FWHM of the PL is considerably broad and spurious features from the laser cannot be distinguished from the emission.

As this occurs even with excellent low pass filter characteristics (for example Thorlabs FELH800 having optical densities (OD) in excess of 6 in the rejection region and > 90% transmission), an excitation geometry with different planes of excitation and emission is preferred. In this case, the excitation laser is focused separately on to the sample at an angle of \(\approx 45^\circ\), and the emission is captured with a separate lens normal to the sample. This is the excitation geometry used in this thesis unless otherwise specified (Chapter 4).
Although the scattered laser light needs to be deflected and properly contained, this configuration tremendously limits the proportion of laser light that is focused into the monochromator, minimising parasitic reflections during spectral dispersion in addition to ensuring that sensitive detectors are not overloaded. Chromatic aberration of the optics must additionally be ascertained when optical elements are chosen. In this thesis, biconvex CaF₂ lenses are used for all PL setups.

A Newport femtoWatt photoreceiver enabled PL signal detection either with a 1mm² Si gain chip sensitive at 300nm to 1100nm or an InGaAs gain chip with a sensitivity region at 700nm to 1800nm. Voltage signals in the picoWatt to nanoWatt range can be ascertained by the femtoWatt receiver through careful choosing of resistance and capacitance values, although this means they can be easily overloaded.

In order to distinguish signals in the femtoWatt range, the measurement bandwidth must be restricted with synchronous detection such as the lock-in technique described in Appendix A1. With the reference frequency of the experiment (chopper frequency) set lower than the 750Hz bandwidth of the photodetector, many interfering optical signals and residual noise in the amplifier electronics that occur at the line-power frequency can be hindered, allowing much lower signal levels to be detected.

By default, the single channel detection is set at ‘AC low’ with a gain of 2x10¹⁰ V/A, as the reference frequency of the experiment is low (<200Hz). The AC high can be used if signals are extremely low, but the additional gain and subsequent noise accrued could obscure some spectral features. The detector responsivity curve of the Newport femtoWatt photoreceiver can be found in Appendix A2.

A schematic of the overall setup used to acquire all PL emission signals is shown in Figure 2.3. The closed cycle He system used in low temperature measurements is discussed in Appendix A4. For PLE experiments, the excitation laser source is replaced with another monochromator to select various excitation wavelengths so that the spectral course of the absorption can be derived. Consequently, the correct range of monitor wavelengths is critical in order to reflect the entire domain of spectral energies. The PL and PLE data obtained for the GaSb/GaAs quantum rings is shown in Figure 2.4.
Figure 2.3: Simplified schematic of PL setup

Figure 2.4: PL and PLE spectra of Type-II quantum rings discussed in Chapter 3. The excitation wavelength for the PLE experiment was varied from 650nm to 1100nm
2.2 Streak camera for TRPL measurements

Upon excitation with external energy, the carriers that participate in recombination return to a state of equilibrium within a fixed duration. Although this duration depends on many factors (excitation power, sample temperature etc.), the decay time of luminescence still contains a wealth of information on the semiconductor optical properties. The extremely fast nature of the physical process of luminescence decay nevertheless exact specialised equipment with the ability to capture recombination events that are often in the nanosecond ($10^{-9}$s) and picosecond ($10^{-12}$s) time ranges. In this work, a streak camera is used to measure the luminescence dynamics.

Figure 2.5 illustrates a schematic outlining the overall implementation method of the streak camera. The discussion below will consider the Hamamatsu streak camera system with the femtosecond pulses of a Ti:Saph laser, however external triggers can also be provided for longer sample decays (pg.31).

Figure 2.5: Streak camera operation with an inset illustrating the timing of signals for capturing a decay image (picture adapted from Hamamatsu product manual)

If a mode-locked laser capable of delivering pulses at high frequencies ($\approx 80$MHz) and short pulse widths ($\approx 140$fs) is used to initiate the decay process in the semiconductor
sample, part of the same beam is directed to a photodiode coupled to an oscilloscope to ensure mode-locked pulses have been formed (critical for a manually mode-locked laser). A fraction of the output beam is additionally directed to a PIN diode C1808-03 capable of registering high repetition (<100MHz) pulses with a minimum input power of 1mW to provide a trigger synchronised with the mode-locked laser to the delay unit. The C1097-05 delay unit (0ns to 31.96ns) then allows the timing between the incident luminescence into the streak camera to coincide with the received trigger. Voltage levels of the incident light, trigger signal and sweep voltage are shown in the inset of Figure 2.5.

The photons that are generated in the instant after excitation by the laser pulse are directed into the streak camera where they are converted into electrons by the photocathode (detector sensitivity curve of the S1 infrared-enhanced thermo-electrically chilled photocathode used is provided in Appendix A2.3). When these electrons arrive at the sweep circuit after being accelerated by a high voltage in the accelerating mesh, they are subjected to an additional high sweep voltage, this time across the sweep electrodes. Applying a rapidly varying electric voltage (in the form of a sinusoidal, square or saw wave) to these electrodes modulates the voltage so that the electron beam can hit the phosphor screen at different points in time due to variation in the deflection angles. Before impinging on the phosphor screen however the electrons are introduced into a micro-channel plate (MCP).

A single electron is multiplied to $10^4$ in the MCP as the numerous thin glass capillaries (diameters of 10μm to 20μm) with internal walls coated with secondary electron emitting material promote significant amplification of electrons on impact. Upon collision with the phosphor screen, the electrons are reconverted into photons, where they are categorised based on their instant of arrival and intensity. The luminescence is thus transfigured in both space (wavelength) and time as shown in Figure 2.5. In this way a streak image is produced, with a horizontal axis representing the wavelength of the emission (from signal dispersed by monochromator) and a vertical axis representing time.

Two methods are used to obtain streak images, photon counting and analog integration. In the photon counting method, individual photon events are added up in the frame memory. This method is primarily employed with low intensity signals, as long
acquisition times can provide higher signal to noise ratios. Certain crosstalk effects in the image intensifier and streak tube are also suppressed in the photon counting mode. In analog integration, a number of images from the camera are accumulated in the frame memory up to 16 or 32 bit depth. The short integration time of the mode make it a suitable choice for high signal intensities or unstable emissions.

In this work, background subtraction of the analog integration and photon counting mode was done by obtaining streak images with the same acquisition time as the data but with a closed camera shutter. For the analog integration method, background subtraction could be done directly using the High Performance Digital Temporal Analyzer (HPDTA) user interface software. The background subtraction of the photon counting mode involved converting the tiff image into a matrix, for manual subtraction from the streak image data matrix using OriginLab software.

![Figure 2.6: Various segments of the streak camera unit](image)

In Figure 2.6, the different sections of the streak camera unit are specified. The horizontal blanking unit provides a return sweep adjustment of the high frequency sine wave applied to the sweep circuit. If a sine wave with a different phase is applied to additional horizontal deflection plates, the sweep path becomes elliptical, and the return sweep signal does not overlap with the main sweep signal. This increases the accuracy of high-speed measurements. However, as only the linear segments of the sine wave can
be used for the sweep, the maximum timescale that can be measured is limited to half the sine wave period.

The resolution of the streak camera with the M10911-01 Synchroscan is 2ps, but this could be effectively an order of magnitude higher depending on the temporal measurement range used, streak camera input aperture width and quality of the trigger pulse. With this sweep unit, the maximum time scale that can be measured is 2.2ns.

In addition to the fast Synchroscan sweep unit, a slow-sweep unit is used to measure luminescence of longer time scales. Here, the unit the sweep voltage is a ramp, which means that the entire voltage period is available for modulation. In this case, a direct output of the trigger can be coupled into the streak camera to be coupled with the delay unit, so ensuring that mode-locked pulsed have been formed is not necessary. Beginning at 4MHz, the sweep frequency of the M10913-11 slow single sweep unit can be extended to values as low as 100kHz with external triggers and adequate adjustment of the time scale through the) user interface HPDTA software.

The streak camera input optics determines both the slit width aperture of 0mm to 5mm and the spectral transmission of 40% to 70% at 200nm to 400nm and 70% from 400nm to 1600nm at the output optics. In the digital CMOS camera ORCA-Flash4.0 V327, the images are multiplied according to a 1:0.7 ratio. Subsequently, the images are supplied to a frame-grabber board, before it is transferred to the HPDTA software for real-time analysis and data acquisition. Post-experimental image processing tools such as background and curvature correction can also be done with the HPDTA software.

In Figure 2.7, the overall setup used for TRPL signal measurements is illustrated. An example of decay time acquisition with laser of suitable pulse width and repetition rate is shown in Figure 2.8.
Figure 2.7: Simplified schematic of TRPL setup

Figure 2.8: Example of carrier decay obtained from laser pulses with suitable repetition rate (picture courtesy of K.Gradkowski)
As described above, a suitable trigger pulse is imperative in both the Synchroscan and Slow-sweep mode to facilitate the collection of luminescence decay with the relevant sweep units. The lasers used for TRPL and PL excitation in this thesis are described below:

a) 650nm Picoquant pulsed diode laser

The LDH-P-650 laser diode head provides picosecond pulses at a maximum repetition frequency of 80MHz and is used in conjunction with a PDL 828 Sepia II multichannel picosecond diode laser driver. It has a minimum pulse width of 52ps, and the pulse energy is calculated based on average power and repetition frequency used. For applications requiring much lower repetition rates than provided by the Sepia II driver, (kHz repetition frequencies), the Picoquant laser diode is coupled to a Rohde & Schwarz SMB100A microwave signal generator having output frequencies (100kHz to 40GHz).

The Picoquant laser is triggered by i) Rohde & Schwarz signal generator to obtain temperature-dependent TRPL images in single and 10 layer quantum rings in Chapter 3 and for AlGaAsSb alloy in Chapter 5 and ii) Sepia II driver at maximum repetition rate 80MHz for temperature-dependent PL experiments in single and 10 layer quantum rings in Chapter 3 and of AlGaAsSb in Chapter 5.

b) 638nm Thorlabs laser diode

The continuous wave Thorlabs laser diode L638P200 offers a maximum of 200mW average output power with operating current of 280mA. This TO can laser diode is mounted to a Thorlabs LDM Laser Diode Mount and subsequently integrated with a Thorlabs 1TC4020 Laser diode and TEC controller. The output power can then be controlled by varying the current through the TEC controller. This laser is used for power-dependent PL measurements for single and 10 layer quantum rings in Chapter 3.

c) NKT Photonics Fianium broadband laser

The Fianium laser has a 410nm to 2400nm continuous single mode output. As the output power is strongly dependent on wavelength, calibration at each output wavelength with a power meter is essential to maintain excitation conditions. The fiber laser input is directed to a monochromator to select the excitation wavelength. This laser is used for photoluminescence excitation experiments for the 10 layer quantum rings in Chapter 3.
d) Coherent Chameleon Titanium:Sapphire laser

The automatically mode-locked Chameleon Ultra laser head consists of i) Verdi solid state pump laser with Nd:YVO$_4$ as a gain medium and LiB$_3$O$_5$ as the nonlinear wavelength doubling medium, ii) Piezo-driven mirrors that enable automatic alignment of the cavity with PowerTrack function and iii) Verdi-pumped Ultra Fast (VPUF) head. The VPUF uses a Titanium:Sapphire gain medium and achieves passive modelocking with a saturable absorber system incorporating a Kerr lens. The optical Kerr effect involves the alteration of the refractive index of a material with extremely high light intensities such that the beam is less intense at the middle compared to the edges. The Chameleon Ultra has pulse widths of 140fs, is tunable from 650nm to 1080nm and has a repetition frequency of 80MHz.

The Coherent Chameleon laser is used in TRPL experiments of InGaAsN:H quantum dots in Chapter 4.
3.

GaSb/GaAs Quantum Rings

Following the discovery of Rashba spin-orbit coupling\(^\text{28*}\), a surge of research on material systems with immanent Berry curvatures\(^{29,30,31,32}\) emerged contemporarily. The coveted tuning of geometric Berry phases subsequently brought about substantial interest in quantum rings\(^{33,34,35}\) as its bipartitely connected geometry and rotational symmetry introduced a ready form of Berry phase control in the form of Aharonov-Bohm and Aharonov-Casher effects, leading to their conceptualization as Dirac electrons\(^{36}\) and topological insulators\(^{37}\). More recently, persistent currents in quantum rings have been discovered to comply with conditions for non-Abelian\(^{38}\) statistics permitting fingerprints of Majorana fermions\(^{39}\). Apart from nonferromagnetic spintronics related applications\(^{40}\), the unique topology of quantum rings is also projected to establish avenues for realizing Terahertz detectors\(^{41}\).

Quantum rings with staggered band alignments in particular exhibit unique excitonic interactions as the Coulomb attraction between the electron and hole quasi-particles (as opposed to confinement related effects in Type-I nanostructures) result in distinct carrier dynamics. For instance, the spatial separation of the electrons and holes in

\(^*\text{Spin-orbit coupling that arises from the overall asymmetry of the confinement potential in a crystallographic structure due to compositional profiles, strain etc}\(^{43}\)
Type-II bandstructures create an electrically tunable electron-hole hybridization gap for spin-dependent electrostatic gating\textsuperscript{42}.

\[ d = 23\text{nm} \]

*Figure 3.1: (Left) Sketch of a quantum ring with 23nm diameter and (right) a typical Type-II heterojunction with confined holes (empty circles) and electrons (solid circles) free in the surrounding matrix. The red arrows indicate possible optical transitions*

More specifically, heterojunctions\textsuperscript{42,43} such as InSb/InAs and GaSb/GaAs are excellent options for exploring spin-orbit interactions which occur in narrow bandgap semiconductors with crystal inversion asymmetries of zinc-blende structures. The extended carrier lifetimes of GaSb/GaAs nanostructures have also enabled their implementation in memory devices\textsuperscript{44}, intermediate bands in solar cells\textsuperscript{45} and as gain material in a photonic crystal cavity laser\textsuperscript{46}.

In general, the growth of GaSb/GaAs quantum rings have elicited much interest\textsuperscript{47,48,49} but studies of their emission dynamics have been limited to a single parameter variation\textsuperscript{50} or without evidence of the ring-shape of the nanostructures (such as detection of AB oscillations)\textsuperscript{51}.

The GaSb/GaAs quantum rings in this work (Figure 3.2) are grown by MBE in Lancaster University using a cold-capping method\textsuperscript{52}. Previous work done in Lancaster focused on enhancing the short circuit current in solar cell devices\textsuperscript{53} by extending their photoresponse\textsuperscript{54}, as quantum ring stacks have reduced lateral or threading dislocations\textsuperscript{55} compared to quantum dots. This also included photocapacitance studies to determine the hole distribution in the rings\textsuperscript{56} and two-photon absorption to obtain its sub-bandgap photoresponse\textsuperscript{57}, in addition to cross-sectional STM to quantify the nanostructure species\textsuperscript{58} and effects of hydrostatic pressure on the open circuit voltage\textsuperscript{59}.  

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However, the optical characterisation experiments such as excitation-power dependent \(^{52,60,61}\) PL have predominantly centred on carrier extraction from the quantum rings as part of a solar cell and less on the particular effects of the ring-shape of the nanostructures. For instance, the emission dynamics studies done on the GaSb quantum rings within GaAs/AlGaAs quantum wells\(^{62}\) did not evince an increase of radiative lifetime with temperature specific to the annularity of quantum rings.

If the precise optical properties of GaSb/GaAs quantum rings are to be outlined however, comprehensive optical characterisation of electron-hole dynamics in dense ensembles are essential. In this chapter, two samples: \(i\) ten stacked layers and \(ii\) a single layer of GaSb/GaAs quantum rings are investigated with PL and TRPL spectroscopy techniques.

![Figure 3.2: Structure of samples with 10 stacked layers or single layer of quantum rings](image)

The carrier dynamics in these structures are detailed with varying physical parameters such as thermal energy, free carrier density and magnetic flux density. The ring-like nature of the nanostructures are characterized by their prolonged radiative recombination times with increasing temperatures and the Type-II band alignment is evident from blue shifting in peak positions with excitation powers.

Phase coherent Aharonov-Bohm oscillations in energy and intensity, hitherto unobserved in Type-II quantum ring structures also attest to the robustness of the self-assembled growth. Equally significant is the scalability of the emissive behaviour to a
single layer of quantum rings, demonstrating that a high correlation in physical properties is maintained, despite the drastic reduction in density of nanostructures.

Figure 3.3 shows the cross-sectional and plan view TEM images of the ten layer GaSb/GaAs quantum rings. The cross-sectional TEM image verifies that the growth of stacked layers has been achieved without accumulated strain and its associated defects while the ring-shape of the nanostructure is evident from the plan-view image. In Figure 3.4, the low temperature photoluminescence spectra of single and ten layer quantum rings are shown. There is a slight increase in peak position energies and a more defined wetting layer feature at 1.28eV observed for the ten layer sample. Note that all excitation conditions were maintained where possible.

Figure 3.3: a) Cross-sectional TEM image of 10 layers of quantum rings b) cross-sectional image of a single quantum ring c) Plan view image of quantum rings from 10 layer [Michael Schmidt, Tyndall National Institute]
Figure 3.4: Low temperature photoluminescence spectra of 1 layer and 10 layers of GaSb/GaAs quantum rings

3.1 Temperature dependent PL in 10 layer QRs

Figure 3.5 shows the peak positions of the 10 layer quantum ring ensemble with an inset of the obtained PL spectra with increase in temperature. A 650nm Picoquant laser coupled to a Sepia II driver to operate at 80MHz (pg.31) with power density of 0.77MW/cm² and a spot size of 20µm was used to excite $\approx 3.14 \times 10^4$ quantum rings ($1 \times 10^{10}$ rings/cm² determined with AFM before capping⁴⁵). The data has been treated with Jacobian conversion (wavelength to energy calculation, Appendix A5) on both the $x$ and $y$ axis. This was possible as the slit width (or resolution) of the monochromator was
maintained throughout the experiment. The contribution of the n+ GaAs substrate was also subtracted from the spectra before fitting (Figure 3.17).

![Figure 3.5: Red shift in peak positions of the quantum ring ensemble with temperature increase. The inset shows PL spectra with increasing temperatures.](image)

From the plotted PL data, it is evident that the range in red shift of the peak energy positions from 9K to 150K (14.7meV) extends noticeably from 150K to 250K (74.6meV). This is a direct reflection of monotonic bandgap shrinkage with temperature in most semiconductors and is a superposition of thermal expansion in the lattice and electron-phonon interaction effects. To characterize this reduction, well established laws based on theoretical consideration of these effects are often compared with experimental data from temperature dependent PL experiments.

The PL data is subsequently fitted with three different equations describing the bandgap energy reduction that occurs in parallel with the accumulation of phonons. In
spite of the large density of quantum rings examined, the analysis is expected to provide benchmark values of basic parameters that quantify the bandgap tendency; previous work on self-assembled quantum dots have shown a temperature dependent bandgap reduction that is predominantly dictated by the host material\textsuperscript{63}, without the substantial implications of increased strain fields that might be expected in nanostructures.

The peak position shift was first fitted with Varshni’s \textit{ad hoc} empirical expression,\textsuperscript{64}

\[
E_g(T) = E_g(0) - \frac{\alpha T^2}{T + \beta}
\]

where \(E_g(0)\) = bandgap at 0 K, \(T\) = finite temperature, \(\alpha\) = magnitude of the limiting slope \(-dE_g/dT\) as \(T\) approaches \(\infty\) and \(\beta\) is believed to be proportional to the Debye temperature, \(\Theta_D\).

From Figure 3.5, it is apparent that this expression does not produce a good fit of the experimental data. Despite being ubiquitous in existing literature (largely ascribable to its simplicity), investigation of Varshni’s law suggests an overestimation of phonon dispersion characteristics with temperature for most semiconductors through the \(T^2\) factor and arbitrariness of parameters \(\alpha\) and \(\beta\).\textsuperscript{65}

The Bose-Einstein statistical model considering both absorption and emission of phonons in the system derived by Vina \textit{et.al}\textsuperscript{66,67} was next applied,

\[
E_g(T) = E_B - a_B \left( 1 + \frac{2}{\exp \left( \frac{\Theta}{T} \right) - 1} \right)
\]

where \(E_B - a_B = E_g(0)\), \(a_B\) = strength of exciton-phonon interaction in meV, \(T\) = finite temperature and \(\Theta = h\omega / k_B\), effective phonon temperature in Kelvin.
This model gives a relatively better fit of the data points compared to Varshni’s law as the equation incorporates the proportionality between the average number of phonons in a given mode and its contribution to the $E_g(T)$ dependence$^{65}$. Despite the vanishing dispersion predicted by the Bose-Einstein model in the low temperature region, an acceptable fit of the peak position shift is produced. This is a consequence of the interaction of electrons with long-wavelength phonons which dominate $E_g(T)$ at low temperatures in bulk semiconductors but are minimised in low-dimensional nanostructures smaller than the wavelength of the lattice vibration$^{63,68}$.

The final fitting was done with a four-parameter model, a power function ansatz derived by Pässler having the form$^{69}$,

$$E_g(T) = E_g(0) - \frac{\alpha \Theta}{2} \left[ p \left( 1 + \left( \frac{2T}{\Theta} \right)^p \right) - 1 \right]$$

[3.3]

where $\alpha =$ magnitude of the limiting slope $-dE_g/dT$ as $T$ approaches $\infty$, $\Theta$ effective phonon temperature and $p =$ the exponent that determines the low-temperature asymptote since $E_g(0) - E_g(T) \propto T^p$.$^{70}$

In this model, the power law behaviour of $p$ allows more accurate fitting of the phonon dispersion characteristics in the cryogenic region without being limited by the rigidity of the $T^2$ dependence as in Varshni’s large dispersion model or underestimated with the vanishing dispersion in Vina’s Bose-Einstein equation$^{65}$. The exponent $p$ also gives measure of the degree of phonon dispersion in the semiconductor structures, with $2 < p \leq 3.3$ and $p > 3.3$ relating to intermediate and small dispersions respectively$^{71}$. The values obtained from the fittings are summarized in Table 3.1.
Table 3.1: Summary of fitting parameters with Pässler's general power function ansatz, Bose-Einstein statistical occupation of phonons and Varshni’s law for 10 layers of quantum rings. The parameters obtained from Pässler’s power function fitting for single layer quantum rings are shown in red square brackets.

<table>
<thead>
<tr>
<th></th>
<th>(E_g(0))</th>
<th>(E_B)</th>
<th>(\alpha) (meV/K)</th>
<th>(\beta) (K)</th>
<th>(\alpha_B) (meV)</th>
<th>(\Theta) (K)</th>
<th>(p)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pässler [3.3]</td>
<td>1.0600</td>
<td>1.54</td>
<td>[1.24]</td>
<td></td>
<td>469.5 [362]</td>
<td></td>
<td>3.77 [5.9]</td>
</tr>
<tr>
<td>Vina et al. [3.2]</td>
<td>1.0605</td>
<td>0.491</td>
<td></td>
<td>625</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Varshni [3.1]</td>
<td>1.0599</td>
<td>0.67</td>
<td>375.5</td>
<td></td>
<td></td>
<td></td>
<td>(2)</td>
</tr>
</tbody>
</table>

Based on the analysis above, Pässler’s general power function ansatz achieved the best estimate of physical parameters in the system regardless of the large ensemble of quantum rings studied. The value of \(p = 3.77\) further emphasizes the small degree of phonon dispersion in the system. It is important to note however, that Equation [3.3] is still a generalized analytical expression and therefore exact parameter values of \(p\) and \(\Theta\) cannot be determined.

For instance, the average phonon temperature value obtained is even higher than the Debye temperature for GaAs (344K). In this case, although the bandgap shrinkage behaviour of nanostructures are dictated by the host material, accurate parameter values for nanostructures must nevertheless consider the heterojunction through more detailed analytical methods such as higher-order root representation\(^6\) and the two oscillator model\(^7\) depicting the individual contributions of high and low energy phonon oscillators.

Further analysis was not implemented here since the ensemble studies do not permit a separate treatment of acoustic and optical phonon dispersions. Deduction of renormalization energies of the bandgap at 0K\(^7\) were similarly not an objective, owing to the large density of quantum rings in the ensemble and the scarce set of luminescence energy points at cryogenic temperatures.

In order to perform a thorough analysis of the reduction in the Type-II GaSb/GaAs quantum ring bandgap with increase in temperature, single quantum rings should be
measured with a microphotoluminescence setup ensuring only one quantum ring is optically excited. The temperature variation of the experiment should also be ideally extended beyond the Debye temperature of the host material (344K) so that precise values of the average phonon temperature can be obtained.

Figure 3.6 shows the Arrhenius plot of the 10 layer GaSb/GaAs quantum rings. The fitting for the Arrhenius plot was done according to the equation,

\[ I = \frac{I_0}{1 + A e^{\left(-E_A/k_B T\right)} + B e^{\left(-E_B/k_B T\right)}} \]  

[3.4]

where \( I \) = measured photoluminescence intensity, \( I_0 \) = photoluminescence intensity at 0K, \( A \) and \( B \) = pre-exponential factors usually attributed to the rate of carrier recombination in crystalline semiconductors, \( k_B \) = Boltzmann constant in eV, \( T \) = finite temperature, \( E_A \) and \( E_B \) = activation energies of two thermally activated non-radiative recombination channels (semiconductor system dependent\(^74\))

Despite being originally devised to describe the activation energy of chemical reactions, the Arrhenius plot has been widely used to define the activation energy of defects in semiconductors with increase in temperature and dissociation of excitons in quantum wells\(^75\). The pre-exponential factor is customarily constant as the ratio of the rate of decrease in radiative recombination to the rate of increase in non-radiative recombination with temperature is estimated to be comparative, but some authors apply a varying dependence of \( A \) and \( B \) in unique circumstances where carrier lifetimes (reflecting radiative recombination rates) are enhanced with temperature\(^76\).

It is essential to clarify here that the radiative lifetime of the GaSb/GaAs quantum ring ensemble also increase with temperature\(^\dagger\); the strong double-exponential behaviour however renders the dominance of one type of recombination over the other insignificant.

---

\(^\dagger\) Figure 3.18, Section 3.5
Satisfactory fitting can thus be achieved employing constant pre-exponential factor values.

Figure 3.6: Arrhenius plot of the quantum ring ensemble where the solid blue circles are experimental data, red line is Arrhenius function fit from Equation 3.4 and black dashed lines represent low and high temperature asymptotes and their intersection at $T_C$. The inset on the top right corner is a torus showing the cross-sectional plane based on which the band alignment of the Type-II heterojunction GaSb/GaAs stacked layers quantum ring is drawn in real space ($z$-axis indicates the direction of growth).

The first activation energy $E_A = 7\text{meV}$ ($A = 2.3$), $T_A = 81.2\text{K}$ (from $k_B T_A$) corresponds almost exactly to the characteristic temperature $T_C$, marked at the intersection of the low and high temperature asymptotes on the Arrhenius plot. This is the minimum thermal energy needed to trigger a significant degree of non-radiative recombination centres in the system. From the PL spectra in the inset of Figure 3.5, it is observable that above 75K, the wetting layer luminescence is fully quenched, and the photoluminescence...
of the quantum rings drops to half its initial intensity. The comparatively low value of \( E_A \) is attributed to the large density of nanostructures, which increase the probability of exciting non-radiative centres such as dislocations, vacancies and interstitial defects in the 7.8% lattice mismatched GaSb/GaAs heterojunction.

The value of \( E_B = 46.5 \text{meV} \quad (B = 163), \quad T_B = 539.6 \text{K} \) on the other hand is too high to be directly related to the external thermal energy supplied to the system and is thus an indication of the energy needed to facilitate carrier transfer from the quantum ring confinement to an existing deep level within the bandstructure.

This energy level is inferred to be the exact energy difference between the ensemble and the local maxima of its localized defect states at \( \approx 75 \text{K} \). The low energy exponential tail\(^7^7,\quad 7^8\) of the PL spectra that produces the asymmetric lineshape is a manifestation of Anderson localization\(^7^9,\quad 8^0\) brought about by fluctuations in the alloy material composition with substantial difference in potentials (As and Sb).

In general, Stranski-Krastanow growth is a two-step process, where the formation of individual nanostructures from accumulated islands is preceded by a balancing of the deposited material through surface diffusion kinetics. As such, bimodal size distributions are frequently encountered\(^8^1,\quad 8^2,\quad 8^3,\quad 8^4\) and are heavily dependent on particular aspects of the growth recipe and other material specifications.

By virtue of this property, a myriad of local minima in the GaSb potential well ineluctably arises in large densities of self-assembled GaSb/GaAs quantum rings through the combined effects of surfactant characteristics in Sb\(^8^5\) during As-Sb exchange and reduced surface diffusion lengths due to the absence of growth interruption techniques\(^8^6\). The ensuing crystalline disorder results in repeated scattering of the hole wavefunctions upon confrontation with irregularities comparable to their wavelength.

With the consequent loss in velocity, the narrow hole wavefunctions generate a static level within the bandstructure (dashed square representing \( E_B \) in inset of Figure 3.6). Though lying mostly dormant at low temperatures, the advent of phonons which provides holes within the quantum ring ensemble the necessary momentum to escape into
its potential trap ultimately establishes this localized defect state level as a channel for non-radiative recombination at higher temperature.

Additionally, the non-radiative implications of Auger recombination must be taken into account. In semiconductors, the energy attained by an e-h pair can be transferred to another electron or hole in the conduction or valence band, depending on bandstructure formation. Upon the creation of an e-h pair, the hole can transmit its kinetic energy to another hole in the spin-split off band, or CHHS (Conduction band-Hole-Hole-Spin splitoff) Auger recombination, speculated in narrow bandgap materials with large spin splitoff energies such as GaSb. Such processes albeit negligible in highly crystalline self-assembled quantum dots with ultrafast recombination times due to their long relaxation timescale (ns to µs), are undoubtedly relevant for the quantum ring ensemble in view of its carrier decay time range.

The breakdown from the conservation of quasi-momentum perpendicular to the heteroboundary precipitated by Auger effects exacerbates the escape of holes from their confinement with temperature increase. As seen above, the energy required for this transition in the stacked layers of quantum rings is derived as $E_B = 46.5\text{meV}$ or the energy difference between the ground recombination state of the quantum ring ensemble and their localized defect states at $\approx 75\text{K}$. Note also that the recombination rates $A$ and $B$ from the Arrhenius equation fit increase by two orders of magnitude between $E_A$ and $E_B$ signifying an abrupt shift in the prevailing non-radiative channel after the threshold temperature of $\approx 81.3\text{K}$.

In Figure 3.7, a temperature dependent increase of the energy difference, $\partial E$ between the local maxima of the quantum ring ensemble and their localized defect states is plotted, with the top left inset marking $Q_r$ (Quantum ring) and $L_{Q_r}$ (Quantum ring localized defect states).

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$^1 0.15\mu$s at 9K, Figure 3.19, Section 3.5
Figure 3.7: Increase in energy difference between the quantum ring ensemble and quantum ring localized defect states with temperature (spline fit is a guide to the eye). The top left inset shows Gaussian peak fits of features represented by local maxima in the PL spectra, and the bottom right inset depicts the trend in FWHM of the quantum rings, Qr and their localized defect states, LsQr with increase in temperature.

The initial 43meV energy difference (first green circle in Figure 3.7) between Qr and LsQr at 9K increases to 47meV ($E_B$ value obtained above) at 75K, and finally to 153.7meV at 250K. $\delta E$ also increases with temperature as vibrational energy increase in the lattice push Qr and LsQr states further apart.

Additionally, the FWHM of Qr broadens by 15meV and LsQr by 37meV from 9K to 150K. After 150K, the FWHM increases by 77meV for Qr and 35meV for LsQr states until 200K, following which there is an abrupt thermal escape of carriers to Qr. This drastic increase in carrier thermalisation after 150K coincides with the notable red shifting of the peak positions in Figure 3.5.
Figure 3.8: Carrier transfer between the wetting layer and the wetting layer localized defect states with increase in temperature. The left inset shows the red shift in peak positions until 50K, before complete thermal quenching, whereas the top right inset shows the exponential fits to the low-energy tails in the quantum ring and wetting layer PL peaks. The discrepancy at the end of the wetting layer exponential fit is due to the substrate subtraction.

This analysis is also compatible with the wetting layer WI (Wetting layer) and LSWI (Wetting layer localized defect states) presented in Figure 3.8, where the carrier transfer from LSWI into WI states with increase in temperature is characterized by the FWHM behaviour up to 50K. The exponential fit to the low energy tails, characteristic of Anderson localization discussed above are shown in the semilogarithmic plot of the PL spectra of the Qr ensemble in the top right inset of Figure 3.8.
3.2. Temperature dependent PL in single layer QRs

In Figure 3.9, the temperature dependent PL data of a single layer of GaSb/GaAs quantum rings is shown with power function and Bose-Einstein fits from Equation 3.3 and Equation 3.4 (Varshni fits not included since they were established to be a poor fit of the data). The excitation conditions were maintained and obtained parameter values from the peak position shifts fitted with Passler’s power function are included in Table 3.1. The noticeable plateau at the low temperature region corresponds to the diminished phonon dispersion ($\rho = 5.9$) attributed to the relative lack of phonons in the single layer quantum rings.

Figure 3.9: Red shift in peak positions of the single layer quantum ring ensemble with temperature increase. Black circles are peak position points of the 10 stack layers drawn for comparison. The inset shows the increase in FWHM of $Q_r$ and $L_{sQr}$ in the single layer quantum rings with temperature.
The magnitude of the limiting slope at $\alpha = 1.24\text{meV/K}$ does not differ by orders of magnitude with $1.54\text{meV/K}$ obtained for the 10 layer sample, suggesting that at higher temperatures, the thermal-lattice expansion between the two samples are comparable. In this case however, the average phonon temperature is closer in value to the Debye temperature of GaAs, probably due to a higher GaAs to GaSb ratio in contrast to the sample with 10 layers.

Carrier thermalisation trends similar to Figure 3.7 are also evident from the FWHM of Qr and $L_{SQr}$ depicted in the inset of Figure 3.9. Here, the FWHM of $L_{SQr}$ increases from 120meV to 186meV until 175K, after which the carriers abruptly escape to the Qr confinement such that there is a sharp increase in Qr FWHM from 150K (90meV) to 225K (165meV). At 250K, a slight reduction in the Qr FWHM is apparent, indicating further thermal escape of carriers from this secondary confinement.

Activation energies of $E_A = 9\text{meV}$ and $E_B = 75\text{meV}$ were obtained from the Arrhenius plot of single layer Qrs shown in Figure 3.10. Again, the first activation energy $E_A = 9\text{meV}$, $T_A= 104.4K$ (where the recombination rate $A = 4.5$) corresponds almost exactly to the characteristic temperature acquired from the intersection of low and high temperature asymptotes. Although the minimum temperature needed to thermally activate non-radiative recombination centres is higher as the reduced layers contains less defects, the values do not scale linearly by the number of stacks.

Considering the tenfold increase in nanostructure density however, a $\approx 20K$ difference in $E_A$ values between the two samples do not seem considerable. The difference in $E_B = 75\text{meV}$, $T_B = 870K$ ($B = 163$) is nevertheless more consequential. At approximately twice the value, the much higher energy needed for Qr states to escape their confinement implies that the single layer system is more resistant to temperature changes as the reduced density of localized defect states promote less carrier escape through $L_{SQr}$ states.

However, the value of $E_B$ coincides with the energy difference between Qr and $L_{SQr}$ at 75K in both samples. The similarity in the range of energy difference (40meV to 160meV) further verifies that the mode of thermionic emission of carriers in the GaSb/GaAs Qrs is the same despite the increased layers (through the CHHS Auger
The recombination rate augmentation by two orders of magnitude once more indicates the abrupt transition in the temperature dependent carrier transfer mechanism. Note also that the values are compatible with the 10 layer sample, \( A = 4.5(2.3) \) to \( B = 160 (163) \).

Figure 3.10: Arrhenius plot of the quantum ring ensemble with blue circles representing experimental data and black dashed lines representing low and high temperature asymptotes and their intersection at \( T_c \). The inset shows the energy difference between \( Q_r \) and \( L_{S,Q_r} \) peaks with temperature and the PL spectra (purple lines) illustrate the abrupt carrier transfer through the sudden asymmetry in lineshape from \( Q_r \) to \( L_{S,Q_r} \) between 50K and 75K.

From the exposition above, it can be justly inferred that there is a transition in the dominant mechanism catalysing thermal quenching of photoluminescence intensity in the quantum ring ensemble from lattice imperfections in the GaSb \( Q_r \) at low temperatures to the thermionic emission of carriers out of the GaSb potential well via non-radiative Auger
recombination at higher temperatures. The localized defect states can thus be likened to a ‘drain’ for radiative recombination in the quantum ring ensemble, as they facilitate the escape of holes out of confinement even with relatively low thermal energy gain (an order of magnitude less than the 450meV\textsuperscript{91} barrier height in a GaSb/GaAs system).

#### 3.2 Excitation Power dependent PL in 10 layer QRs

![Absorption curve of 10 layer quantum rings with photoluminescence excitation experiments. The inset shows how the low energy tail becomes more pronounced at lower excitation energies](image)

In Figure 3.11, the absorption curve of the quantum ring ensemble mapped from experimental data of photoluminescence excitation (PLE) experiments is drawn with an inset showing PLE spectra excited with wavelengths of 1.409eV to 1.333eV. The Fianium
tunable broadband supercontinuum laser excitation source was varied from 1.25eV to 1.9eV (990nm to 660nm) and filtered by a monochromator before being directed to the sample. All data were taken at sample temperatures of 7.6K and the excitation power was maintained at 0.1mW for all excitation wavelengths. The two discontinuities in the absorption curve are induced by excitation with energies lower than GaAs (1.53eV) and wetting layer (1.33eV) respectively.

From the absorption curve, it is apparent that the majority of free e-h pairs are created in the GaAs layers. At excitation energies lower than the GaAs bandgap, there is a conspicuous drop in intensity which continue systematically with subsequent reduction in excitation energies until 1.33eV. At lower excitation energies, the probability of recombination from the quantum ring localized defect states, LsQr also increases as less phonons are required to match the conservation of momentum for recombination. This results in a strongly asymmetric lineshape, with the lower energy exponential tail becoming more pronounced with decreasing excitation energies (inset of Figure 3.11).

The asymmetric lineshape is a testament to the lack of interaction between Qr and LsQr states at low temperatures, justifying the requirement for externally supplied thermal energy as seen above to facilitate carrier transfer. Additionally, the quenching of PL intensity at excitation energies of 1.25eV suggest that significant electron-hole pair creation does not occur in the quantum ring or wetting layer.

Excitation power dependent PL data presented in Figures 3.12, 3.13 and 3.14 were done at low temperatures of 8.5K with a Thorlabs diode laser having a continuous wave output at 638nm. PL spectra at low and high excitation powers are plotted in Figure 3.12, with peak positions and FWHM of quantum ring and wetting layer plotted separately in Figure 3.13 and 3.14.

The light blue curves in Figure 3.12 are obtained with excitation powers of 25µW, 50µW, 75µW, 100µW and 250µW whereas the dark blue curves are spectra with excitation powers of 5000µW, 7500µW and 10000µW. An 8x surge in signal intensity with increasing excitation powers prompted a monochromator slit width closure from 2000µm to 250µm between 25µW and 10000µW; however, the broad linewidth was not affected by altered resolution. Having confirmed that most free carriers are created in the
GaAs layers, the unflagging intensity gain without plateau with increasing excitation power is directly indicative of a continuous supply of $e$-$h$ pairs through the abundance of GaAs material, and a sufficient volume of quantum ring and wetting layer states. In addition, the blue shift of the spectra with increasing excitation power confirms the Type-II bandstructure of the system.

Figure 3.12: PL spectra of 10 layers of GaSb/GaAs quantum rings at low excitation powers (light blue) and high excitation powers (dark blue). The inset shows the contrast between localized defect states behaviour of $Ls_{Qr}$ (downward arrow) and $Ls_{WL}$ (upward arrow) with increasing excitation powers

In the inset of Figure 3.12, the normalized intensity and normalized peak position (to $Qr$) of the power dependent spectra is illustrated to scrutinize the characteristics of localized defect states in the low energy tail of the quantum ring ensemble and the wetting layer. At low excitation powers of 10µW to 250µW (black curves), the low energy tail ($Ls_{Qr}$) narrows steadily until 250µW, after which there is no difference to the lineshape
(grey curves). Conversely, the low energy tail of the wetting layer \((L_{SW1})\) fills out after 250\(\mu\)W with continuous increase in excitation power. This contrast in behaviour can be traced to the structural morphology of the quantum rings and wetting layer states.

In the case of quantum rings, the self-assembled growth, capping method precipitating ring formation and large density of nanostructures collectively introduce a substantial range in the localization potential of the localized defect states, \(L_{Qr}\). Until excitation powers of 250\(\mu\)W, the more weakly bound localized defect states escape their confinement with the increasing hole-hole repulsion, leaving behind only strongly bound \(L_{Qr}\) states that are unaffected with further surge in free carrier densities.

On the other hand, the behaviour of the low-energy tail of the wetting layer localized defect states, \(L_{SW1}\) is characteristic of continuous density of states (DOS) occupation in a localized potential. Here, the quantum well-like nature of the wetting layer allows a uniform increase in the population of \(L_{SW1}\) states up to the mobility edge\(^{79}\) until the states are completely filled. The unchanging PL lineshape also demonstrates minimal interaction between the potential wells of the Qr and Wl with increasing free carrier density.

The substantial blue shift in peak positions with increasing excitation powers in Type-II systems is commonly attributed to a single underlying mechanism such as band-bending\(^{92,93}\) state filling\(^{94}\) and capacitive charging\(^{95,96}\). In the stacked layers of GaSb/GaAs quantum rings, there is nevertheless a distinct transition in the power law behaviour of the peak positions from capacitive charging in the low excitation regime to band bending in the high excitation regime as shown in Figure 3.13.

Coulomb attraction with confined holes enables the surrounding electrons to easily occupy lower energy states in the capacitive charging model. In Type-II systems, the long recombination times due to reduction in electron and hole wavefunction overlap additionally allow ready occupation of higher energy states. With the influx in free carriers, the increasing hole population in the confines of the GaSb Qr generates hole-hole repulsion which the electron must now simultaneously contend with in order to fill the higher-level states. Capacitive charging has been predicted to result in a \(P^{1/2}\) shift of the peak position\(^ {95,96}\) in nanostructures.
Figure 3.13: Excitation power dependent plot of 10 layers of quantum rings. The inset shows the FWHM of $Q_r$ and $L_sQ_r$ under the same increase in excitation.

Beyond excitation powers of 250µW however, the excitonic recombination governed by many-particle Coulomb interaction effects between electron and holes yield to radiative recombination dominated by charged excitonic multiplexes due to the high density of free carriers. Here, the spatial separation of carriers result in a dipole layer formation at the interface of the heterojunction, with electrons experiencing quantization in energy akin to a triangular potential well with applied electric fields\(^97,98\). The bending of the bands with increasing excitation powers thus results in a blue shifting of the peak energy position by $P^{1/3}$ until 10000µW, a trend which has been widely reported in Type-II heterojunctions\(^99,100,101\). In total, the quantum rings blue shift by 32meV (12meV blue shift with capacitive charging and 20meV blue shift with band bending).
Although broadening of the FWHM is conventionally reported with increasing excitation powers in single nanostructures\textsuperscript{102} due to an efflux of carrier-phonon interactions effects, the criteria for such spectral diffusion are nonetheless averaged out in stacked ensembles of quantum rings.

In these circumstances, the narrowing of the FWHM in Qr with excitation powers by 34meV from 25µW until 250µW before the onset of saturation (FWHM differs by only 5meV from 75µW to 10000µW) is consistent with hole-hole repulsion effectively expelling hole states from shallowly confined quantum rings with increasing free carrier density. Likewise, the FWHM of Ls\textsubscript{Qr} states tapers drastically by 70meV from 25µW to 100µW compared to the 20meV decrease from 250µW to 10000µW. Note also that this reduction in FWHM as a result of hole-hole repulsion in both Qr and Ls\textsubscript{Qr} states are parallel with the capacitive charging regime shown in the inset of Figure 3.13.

The blue shifting in wetting layer peak positions in Figure 3.14 up to 1000µW indicates the Type-II nature of the wetting layer band alignment, although the absence of a power law trend suggests a substantial gradient at the heterojunction of Wl and GaAs. At excitation powers beyond 1000µW, the Wl states are completely filled, and the peak positions experience a plateau until the increase in sample temperature at 10000µW incites a red shift in energies denoting a reduction of the wetting layer bandgap.

In the inset of Figure 3.14, the sharp narrowing of wetting layer FWHM at lower excitation powers can again be attributed to the escape of weakly bound Wl hole states due to hole-hole repulsion. Unlike the Qr ensemble however, the emptying of Wl states is accompanied by a filling of Ls\textsubscript{Wl} states from 100µW to 10000µW. As discussed above, Ls\textsubscript{Wl} state-filling is characteristic of continuous DOS occupation in a localized potential. More energy states are thus available for the localized defect state levels for carrier transfer and trapping from Wl to Ls\textsubscript{Wl} until 7500µW, after which the thermal energy gained culminates in an abrupt carrier transfer from Ls\textsubscript{Wl} to the Wl states at 10000µW.
Figure 3.14: Excitation power dependent plot of the wetting layer in the 10 stacked layers of quantum rings. The inset shows the FWHM of $W_l$ and $L_{SW_l}$ under the same increase in excitation.
3.4 Excitation Power dependent PL in single layer QRs

Figure 3.15: Excitation power dependent plot of single layer quantum rings, where the grey data points and fits corresponding to the right y-axis are the peak position shifts of the 10 layers of quantum rings drawn for comparison. The inset shows the FWHM of Qr and LsQr under the same increase in excitation.

This analysis is also consistent with the peak position behaviour of the Qrs in the single layer sample in Figure 3.15; a linear progression from capacitive charging in the low excitation regime succumbs to band bending at higher excitation powers. The peak positions blue shift by 35meV with capacitive charging (excitation powers 10µW to 75µW) and 23meV with band bending (excitation powers 75µW to 10000µW).

Here, although the shifts with band bending are similar between the samples (20meV for the 10 layers of Qrs), capacitive charging values are almost thrice the value in the single layer sample. This is related to the extremely shallow confined Qr and LsQr states in the dense 10 layer sample that are unable to contribute to effective charging and
escape their confinement at very low powers of 10µW (in the inset of Figure 3.13, the first data point of $L_{SQR}$ does not match the capacitive charging trend).

From 10µW to 100µW, the FWHM of the $Q_r$s in the single layer sample decreases by 69meV, and upon cessation of most hole-hole repulsion in the shallow $Q_r$ states, the FWHM decreases by a mere 6meV from 100µW to 10000µW as depicted in the inset of Figure 3.15. The FWHM of $L_{SQ_r}$ on the other hand decreases by 50meV at an almost steady pace from 10µW to 10000µW.

### 3.5 Temperature dependent TRPL in 10 layer QRs

![Image](image.png)

*Figure 3.16: (Top) Combination of streak images at 9K capturing the entire range of quantum ring ensemble emission, where the white dashed lines mark the double-exponential behaviour of the decay with excitation pulse in the top left corner. (Bottom left) The red curves represent PL spectra at 9K with windows showing windows used for decay curve extraction. (Bottom right) Mono-exponential emission decay of the $Q_r$ ensemble at 150K.*
Time-resolved photoluminescence spectroscopy (TRPL) experiments were carried out to investigate the carrier lifetime in the stacked layers of Qrs. The eight combined streak images in Figure 3.16 (each streak window captures a range of 80nm) at 9K from 650nm to 1300nm and the bottom right inset of the quantum ring ensemble peak at 150K were measured using the same excitation conditions. The decay of the Picoquant 650nm excitation laser pulse is shown at the top left corner of the image for comparison. The PL spectrum at 9K (red curve) identifies the three spectral features observed in the streak image. The 80nm and 20nm boxes drawn on the quantum ring and wetting layer peaks represent the decay curve extraction window of the respective features.

The apparent merging of the wetting layer and quantum ring ensemble emission is in fact the luminescence decay of the n+ GaAs substrate. Carrier lifetime values of 43ns at 9K to 100K (Figure 3.17) were obtained by measuring the exact substrate used in the MBE growth of stacked layers of quantum rings without any additional layers. Considering that this value remains almost constant in the temperature and wavelength range where bifurcations in the carrier decay trends are observed, the influence of the substrate emission on carrier lifetime analysis of the quantum rings is inconsequential.

Figure 3.17: (Left) PL spectra before and after subtracting the contribution of the n+ GaAs substrate (Right) Decay curves of the n+ GaAs substrate from 9K- 225K. The inset shows PL spectra of the n+ GaAs substrate in the same temperature domain.
Similar magnitudes and double-exponential decay characteristics of the wetting layer and quantum ring ensemble are discernible based on qualitative observation of Figure 3.16. In order to unravel the complex carrier dynamics in the stacked layers of quantum rings, TRPL measurements at low temperatures were extended to include data with increasing sample temperatures. Figure 3.18 shows the decay curves from 9K to 75K of the quantum rings with an inset of the wetting layer decay curves at 9K and 50K.

![Figure 3.18: Decay curves of the quantum ring ensemble from 9K to 75K displaying contrasting behaviour in $t_r$ and $t_{nr}$. The inset shows decay curves of the wetting layer at 9K and 50K.](image)

The downward arrow represents the diminishing trend of the first time component, $t_{nr}$ resulting from an escalation of carriers recombining through non-radiative centres in the lattice whereas the upward arrow marks the contrast in radiative recombination behaviour of the second time component, $t_r$. Decay times of $t_{nr}$ and $t_r$ are then extracted and plotted up to the highest recordable temperature of each.
Figure 3.19 exhibits the trends of both time components from 9K to 250K. For $t_{nr}$ on the right axis, the 0.038μs decay time drops steadily to 0.01μs with temperature until 150K, after which the signal to noise ratio decreases and decay time fitting becomes mathematically unreliable. The decay curves then become mono-exponential and represent only $t_r$. Principally, the reduction in carrier lifetimes with rising sample temperatures is unsurprising as non-radiative recombination centres are activated through the gain in lattice vibrational energy (seen above with activation energies $E_A$ and $E_B$).

![Figure 3.19: Extracted radiative (left y-axis) and non-radiative (right y-axis) decay times. The inset shows the exact dependence of radiative lifetime as a function of temperature, $T$ from 9K to 140K.](image)

It might appear incongruous however that non-radiative decay affects observable luminescence in decay curves extracted from streak images (usually represented by the equation $\tau^{-1} = \tau_r^{-1} + \tau_{nr}^{-1}$). This concept can be comprehended if all excited carriers are visualised in the instant after the excitation pulse as water in a tank with a tap. If a leak exists from a hole at the bottom of the tank (non-radiative channel), the rate of water flow...
from the tap (radiative channel) is altered even though the water leakage is not directly measured.

On the other hand, the radiative recombination time, \( t_r \) (left axis in Figure 3.19) experiences a consecutive increase from 0.15\( \mu \)s to 0.476\( \mu \)s from 9K to 125K, followed by a drastic drop to 0.158\( \mu \)s at 150K and finally to 0.097\( \mu \)s at 250K. The temperature dependent carrier decay time is ascribed to \( i \) the band alignment in the GaSb/GaAs heterojunction, \( ii \) quasi one-dimensional density of states due to the annularity of quantum rings and \( iii \) the density of excited free carriers.

Extended carrier lifetimes are generally anticipated in semiconductor systems with Type-II (staggered band) alignments as minimized overlap between the spatially separated electron and hole wavefunctions lowers optical transition probabilities. Notwithstanding this accepted precept, carrier lifetimes measured in Type-II GaSb/GaAs quantum dots have shown values in the range of 20ns\(^{103,104,105} \), necessitating further justification of the substantial surge in the values observed for the quantum ring ensemble.

Consideration of the ~1D confinement characteristics of the quantum rings then becomes crucial, as the possibility of revolving motion in both quasi-particles of the exciton with different trajectory radii postponing their recombination could extend the instance of carrier decay. In addition to this, the excitation power density (11.5kW/cm\(^2\)) used to capture the emission dynamics is a critical factor in determining radiative decay times since low excited carrier densities quickly lead to an exhaustion of available electrons around the ring with continued recombination. As a result, the wavefunctions of confined holes and electrons further away in the matrix are forced to contend with decreased overlaps, prolonging their recombination times possibly up to two orders of magnitude\(^{106} \).

With the enhancement in mobility induced by applied thermal energy from 9K to 125K, the already low probability of carrier recombination is reduced even more as momentum provided by the phonons cause the carriers to experience kinetic energy, reducing Coulomb confinement and thus the wavefunction overlap (graphically represented below in Figure 3.20). Moreover, the non-radiative recombination channels
(shown as arrows marked $t_{nr}$ in the inset of Figure 3.6) activated with temperature act as traps for the carriers, effectively destroying their prospects of recombining radiatively.

These cumulative effects produce a consistent increase of radiative recombination times, similar to that previously reported in quantum wells$^{107}$, single Type-I quantum rings$^{108}$ and Type-II hetero nanoplatelets$^{109}$. After 125K however, the exciton-phonon coupling dominates and there is a sharp drop in lifetime which continues with subsequent temperature increase until there is no more detectable signal.

![Figure 3.20: Reduction in overlap between electron and hole wavefunctions with increasing temperatures from left to right, leading to extended radiative recombination times](image)

Apart from this, details on the density of states (DOS) profile adopted for carrier recombination can be identified from the exact propensity of carrier lifetime increase (inset of Figure 3.19). In the domain of 9K to 125K, the initial $T$ dependence is impelled by a 2D-like density of states (DOS) profile attributed to the spreading of hole wavefunctions in the wetting layer in self-assembled nanostructures$^{110,111}$. After 50K, this behaviour transitions into a $T^{1/2}$ dependence characteristic of a 1D DOS$^{112}$, as the wetting
layer states are now completely extinguished (Figure 3.8). This perceptible shift in behaviour demonstrates that the influence of the wetting layer on the optical properties of nanostructures grown by self-assembly should not be neglected.

### 3.6 Temperature dependent TRPL in single layer QRs

Although Wl dynamics cannot be detected in the single layer quantum rings, the carrier lifetimes were measured under similar excitation conditions to draw a parallel with the 10 layer system. The duality of trends in the radiative and non-radiative carrier lifetimes with increasing temperatures illustrated in Figure 3.22 indicate the scalability of their transient dynamics. In this case however, carrier lifetimes could not be obtained beyond 100K, due to the lack of signal intensity for streak camera measurements under similar excitation conditions (a comparison is shown in Figure 3.21).

*Figure 3.21: Streak camera images of quantum ring emission for one layer (left) and 10 layers (right) at 9K. All excitation parameters were maintained*
Figure 3.22: Decay curves of single layer quantum rings from 9K to 75K. The inset shows the plot of extracted radiative and non-radiative decay times

Despite this, carrier lifetimes are recorded to increase from 9K to 75K from (0.22μs to 0.583μs). At 100K, there is a drastic decrease to 0.18μs and the section of the decay curve representing non-radiative recombination times cannot be extracted. The 0.07μs and 0.107μs extension in carrier lifetime at 9K and 100K (highest recordable lifetime) in the single layer Qrs is expected to be the result of the limited density in LSub states. However, the sharp surge in phonons at 80K results in a sudden escalation of exciton-phonon coupling, leading to a curtailment of radiative recombination as observed above with temperature-dependent PL experiments (Figure 3.10).
3.7 Magnetic field dependent PL in 10 layer QRs

In addition to its influence on the carrier dynamics of the system, the annularity of nanostructures in the stacked layers of GaSb/GaAs quantum rings advocates their suitability for observation of the Aharonov-Bohm (AB) effect.

The geometric phase acquired in holonomic systems extends to quantum mechanics in various forms such as in the polarization of light waves\textsuperscript{113}, quantum Hall effect\textsuperscript{114} and in the exchange statistics of spins\textsuperscript{115}. In condensed matter physics, the geometric phase can be amassed by the electron Bloch state as it traverses the first Brillouin zone if a crystalline periodic lattice is considered. In the case of a 3D lattice with inversion symmetry, the non-trivial geometric phase accompanying the Bloch electrons is defined as the sum of the overall phases in the individual and occupied energy bands, known as the Zak phase\textsuperscript{116}.

The geometric phase of electronic Bloch states contains a gauge-dependent parameter (known as the Berry connection) and is thus not physically observable. The curl of the Berry connection (or Berry curvature) on the other hand is an experimentally acquiescent parameter as it is gauge-invariant\textsuperscript{117}. As the curl of the electromagnetic vector potential is equivalent to the magnetic field applied perpendicular to a closed loop, experiments exploiting these properties can reveal incidences of quantum mechanical manifestations of the geometric Berry phase in condensed matter physical systems.

Previous predictions by Aharonov and Bohm regarding the relative phase acquired by a charged quantum particle in the presence of a non-zero magnetic vector potential\textsuperscript{118} was subsequently marked as a special case of non-local geometric phase acquisition by Berry’s mathematical formalism\textsuperscript{119}. After the first successful experimental demonstration in electronic wavepackets completely shielded from magnetic fields\textsuperscript{120}, the Aharonov-Bohm (AB) effect has been observed in sub-micron metal rings\textsuperscript{121}, iron whiskers\textsuperscript{122}, mesoscopic rings\textsuperscript{123}, topological insulator\textsuperscript{124} and Dirac semimetal\textsuperscript{125} nanowires, carbon nanotubes\textsuperscript{126}, and most recently in quantum Hall edge modes\textsuperscript{127} and ion traps\textsuperscript{128}.
In a crystalline semiconductor, the Aharonov-Bohm effect is the quantum interference between energy eigenstates of one Hamiltonian that in the presence of a magnetic flux gains a relative phase as it adiabatically revolves around a closed loop and one that does not. Although the effect is topological, some form of intrinsic polarizability of carriers should nevertheless be contained in the system as only relative phase differences can be detected experimentally.

The advances in growth and fabrication techniques have enabled achievement of a variety of semiconductor systems with inherent structural morphologies with marked variation in trajectory of the individual quasi-particles. Nanostructures with ring-like geometries are therefore desirable, as the toroidal closed loop system readily encourages the cyclic evolution of the energy eigenstates. However, neutral excitons in semiconductors were not expected to be suitable candidates as the composite neutrality of the particles would prevent the creation of a radial dipole moment and with it, observable interference between the quasi-particle states accumulating differing phases129.

Notwithstanding this fundamental caveat, the finite size of the exciton was predicted to produce a magnetic moment that is sensitive to the magnetic flux change in quantum rings with sufficiently small radii130 and adequate polarization between the quasi-particles of the exciton131. The interference between quasi-particles with varying magnitudes of accumulated geometric Berry phases (in the form of magnetization flux factor) would then evince itself in oscillations in energy and/or intensity with applied external electric field, both perpendicular132 and in-plane133 or in optical experiments. Oscillations obtained from optical experiments are known as the optical AB effect.

Observation of AB oscillations in layers of vertically aligned Type-II quantum dots even up to 180K134, Wigner molecules in Type I quantum rings and recently in a single nanowire135 has established their detection in neutral excitons as a definite plausibility. It is noted nonetheless that oscillations would be extremely difficult to observe if both quasi-particles are confined in the same region such as in Type-I quantum dots.
The excitonic energy state can be considered a function of the orbital angular momentum transition of the individual quasi-particles, which in turn is a direct function of the quantized magnetic flux potential. For systems with weak Coulomb correlation between the quasi-particles, this is written as\footnote{131},

$$E_{\text{exc}} = E_g + \frac{\hbar^2}{m_e R_e^2} \left( l_e + \frac{\Phi_e}{\Phi_0} \right)^2 + \frac{\hbar^2}{m_h R_h^2} \left( l_h + \frac{\Phi_h}{\Phi_0} \right)^2$$  \[3.5\]

where $E_g$ includes the energy of the bandgap and confinement energies independent of magnetic field, $\hbar$ is the reduced Planck’s constant, $\Phi_0 = \frac{hc}{e}$, and $R_e$, $m_e$, $l_e$, $\Phi_e$ and $R_h$, $m_h$, $l_h$, $\Phi_h$ are the radii of trajectory, effective masses, angular momenta and accumulated magnetic flux of the electron and hole quasi-particles respectively. The magnetic flux $\Phi_e(h) = \pi R_e^2/R(h)B$ describes the quantum geometric Berry phase accumulated as the quasi-particles traverse their individual trajectories, as described above.

If the electron and hole in the exciton are strongly Coulomb correlated however, this equation simplifies to,

$$E'_{\text{exc}} = E'_g + \frac{\hbar^2}{2M R_0^2} \left( L + \frac{\Delta \Phi}{\Phi_0} \right)^2$$  \[3.6\]

where $L = l_e + l_h$, $R_0 = \frac{(R_e + R_h)}{2}$ and $M = \frac{(m_e R_e^2 + m_h R_h^2)}{2}$. In this case, the magnetic flux is computed through the area between both the particle trajectories, $\Delta \Phi = \Phi_e - \Phi_h$ so the earlier flux term becomes $\pi(R_e^2 - R_h^2)B^{136}$.

In the presence of externally applied magnetic flux, the change in the relative phase of the electron and hole owing to a difference in their concentric trajectories is then expected. This leads to observable oscillations between the bright and dark excitonic transitions as the excitonic ground state changes to states of higher orbital angular momentum.

The stacked layers of Type-II GaSb/GaAs quantum rings are thus predicted to evince oscillations pertaining to the optical AB effect as the spatial separation of electron
and holes permits the existence of radial dipole moment\textsuperscript{131,134,137}. With increasing magnetic fields, the electron wavefunction is pushed closer and closer to the boundary of its confinement, increasing its potential energy such that at certain magnetic fields it becomes energetically more favourable for it to jump to higher energy states\textsuperscript{138}. As such, the angular momentum transitions are expected to be mostly dictated by the quasi-particle with more freedom in trajectory, which are the free electrons in the GaAs matrix.

In the case of Type-II quantum dots with strongly confined holes, multiple stacked layers were found to be crucial in dictating a ring-like geometry in electron motion\textsuperscript{139,140,141,142}, while also averaging out the size distribution and variation in oscillation radius in the quantum dot ensemble, effectively amplifying the oscillation amplitude. Sufficiently thick spacer layers were also grown so that the exciton does not travel in the $z$ direction\textsuperscript{134}. Here, the quantum rings investigated have inherent ring-like geometry, rendering exact vertical stacking of the nanostructures unnecessary (while still enhancing oscillation amplitudes).

In addition, the gradient in material composition and corresponding ubiquity of L$_{\text{Sr}}$ states in the quantum ring ensemble do not fatally diminish the possibility of observing AB oscillations as quantum coherence effects are found to not be completely extinguished\textsuperscript{143} if the localization of particle wavefunctions are spatially variant. $kp$ calculations (Figure 3.23) of a quantum ring simulated for the structures grown at Lancaster University also show that electron wavefunctions lie outside the quantum rings at the ground state.

Magnetophotoluminescence experiments to detect the presence of optical AB oscillations in the stacked layers of GaSb/GaAs quantum rings were conducted at low temperatures of 4.2K in the Faraday geometry up to a magnetic field of 5T with steps of 0.25T at Wroclaw University of Science and Technology in Poland. A 660nm CW laser diode was used to probe the ground state energy of the quantum ring ensemble peak under low and high excitation powers of 75µW and 750µW. The resulting energy oscillations of the quantum ring peak are presented in Figure 3.25 after subtraction of the average Zeeman splitting shown in Figure 3.24. No oscillations in energy were present in the wetting layer peak.
Figure 3.23: Simulated electron (red) and hole (blue) wavefunction probability densities at the ground state calculated for the first 8 levels. The results show that electrons lie outside the quantum ring at $e_0$. [Multiband $k\cdot p$ simulation courtesy of R.Arkani with relevant results published $^1$]

The amplitude of the undamped oscillations increases noticeably with higher values of magnetic field and the 2.53T period obtained with excitation powers of 75µW increases to 2.92T when excitation powers are increased by an order of magnitude to 750µW. It is noted that the error analysis in Figure 3.25 introduces a range of uncertainty in the determination of different oscillation periods with the increase in excitation power. However, as it is expected that a clear band bending affects the Type-II heterojunction in the high power excitation regime (Figure 3.13), the difference in the oscillation periods will be maintained until verified otherwise with further experiments.

Oscillation periods of 2.5T in Type-I quantum rings (although in intensity) were reported to be suggestive of small ring heights and wide centre openings, where the
excitonic orbital radius was estimated to be 22.5nm\textsuperscript{145} following the frequently applied estimation of the exciton orbit radius from the period of oscillation\textsuperscript{134} \( \partial B = \Phi_0 / \pi R_e^2 \). The exciton orbit radius of the GaSb/GaAs Qrs is consequently calculated to be 22.5nm at excitation powers of 75µW and 21.3nm at 750µW, leading to ring diameters of 40nm.

Figure 3.24: Bandgap energy vs magnetic field data of the quantum ring ensemble at low and high excitation powers before background subtraction. The inset shows the Coulomb correlation of the electron and hole and how the magnetic flux, \( \Delta \Phi \), is computed as the area between the electron and hole radius in trajectory [experiment conducted in Wroslaw University of Science and Technology, Poland]

Structural analysis with plan-view and cross sectional TEM (Figure 3.3) however produce near consistent estimates of 23nm in outer diameter on average. This indicates that the simplified relation above cannot be used to estimate the excitonic orbital radius for the Type-II quantum rings despite the strong Coulomb correlation between the electron and hole and the collective increment of the exciton values to higher orbital
angular momentum with increasing applied magnetic field strengths, discussed above with Equation [3.6].

Figure 3.25: AB oscillations in stacked layers of Type-II GaSb/GaAs quantum rings after background subtraction

Here, the extended exciton wavefunction due to the indirectness of the quasiparticles in real space necessitates a more complex method of determining $R_e$ and $R_h$ (probably as a function of their effective masses\textsuperscript{146}) allowing a more accurate effective excitonic radius to be derived from the period of oscillation. A polarization sensitive photoluminescence experiment would give more insight into this, as the diamagnetic coefficients obtained would exactly represent the degree of wavefunction extension in the nanostructures\textsuperscript{147}. Such experiments would necessitate the growth of site-controlled quantum rings to enable precise PL measurements along different growth axes.

A direct correlation between the excitation power and period of AB oscillations has been previously reported in single Type-I quantum rings\textsuperscript{148} where the spatially
The invariant nature of the confinement resulted in a reduction of the binding energy of the biexciton with increasing excitation power leading to a subsequent decrease in oscillation period.

In the case of Type-II GaSb/GaAs Qrs however, the extension in oscillation period is attributed to a reduced effective excitonic orbital radius, as prominent band bending occurs at the interface of the Type-II heterojunction in the quantum ring ensemble with excitation powers higher than 250µW. Thus, although exact exciton orbital radius values cannot be ascertained from the estimation used above, it is still possible to infer that the decreased oscillation period is a direct result of an increased overlap between the electron and hole wavefunctions.

![Figure 3.26: Intensity vs magnetic field data of the quantum rings and wetting layer before and (inset) after background subtraction at excitation powers of 75µW](image)

Figures 3.26 and 3.27 depict the intensity profile of quantum rings and wetting layer with increasing magnetic field under excitation powers of 75µW and 750µW.
Oscillations in intensity with magnetic field increments are believed to be an interplay between wavefunctions squeezing to the interface and an expansion in electron trajectory with higher magnetic field strengths\textsuperscript{141}. They are also reasoned as a supplementary hallmark of AB oscillations since excitonic transitions to higher orbital angular momentum levels are predicted to intimately affect the oscillator strength\textsuperscript{149}.

Although only states with total momentum of $L = l_e + l_h = 0$ are optically active in excitons with perfect rotational symmetry, deviation from this ideal in self-assembled semiconductor nanostructures\textsuperscript{140} permits radiative recombination of $L > 0$ states with higher magnetic flux densities alongside oscillations in energy.

![Figure 3.27: Intensity vs magnetic field data of the quantum rings and wetting layer before and (inset) after background subtraction at excitation powers of 750$\mu$W](image)

Recalling that the hole wavefunction of the quantum rings extend into the wetting layer at low temperatures (resulting in the DOS profile detected with TRPL experiments in Figure 3.19 above), the auxiliary feature of wetting layer intensity increases with...
magnetic fields (no change in wetting layer energy was detected) must undoubtedly be taken into consideration. The squeezing of the hole wavefunction to the interface of the heterojunction with applied magnetic field thus results in comparable intensity profiles. A correlation between the wetting layer and quantum ring intensities was thus expected at low temperatures especially at the higher excitation power where the effects of band-bending were evident.

Under low excitation powers (Figure 3.26), the intensity of wetting layer and quantum ring increase in an almost parallel fashion, reaching a plateau at higher magnetic field strengths (< 4T). The inset of Figure 3.26 shows the data points after subtraction of the background so that the physical characteristics of the oscillations can be discerned. Here, the intensity profile undergoes abrupt changes in both the quantum rings and the wetting layer but there is not much correlation between them. At higher excitation powers (Figure 3.27), the gain in intensity of the wetting layer and the quantum rings approach similar values at higher magnetic field strengths without any observable saturation at values <4T. In addition, there is a high degree of correlation between the intensity changes in the quantum rings and the wetting layer after background subtraction as shown in the inset of Figure 3.27.

The band-bending at the interface tilts the heterojunction so that the oscillator strength of the quantum rings and wetting layer become almost identical at higher excitation powers. This angled interface enables greater degrees of successive overlap between the electron and hole wavefunctions so that the intensity does not saturate with continuing accretion in magnetic flux densities.

Modelling of the exact energy levels of the exciton with increasing magnetic field strengths is necessary in order to identify the exact higher orbital angular momentum transitions. Accurate modelling is non-trivial however, as it would essentially have to take into account strain, the realistic volcano-like shape of nanostructures (presence of magnetic field at the rim which enhances the electron localization close to the minima of the adiabatic potential)\(^{150}\), presence of impurities\(^{151}\), inhomogeneity of material composition and structural distortion\(^{152}\), size distribution of nanostructures in the ensemble and the Coulomb-dominated nature of the electron, which is difficult/impossible for a lot of
models. The graded interface of the heterojunction in Type-II nanostructures should also not be neglected as it alters the angular momentum periodicity\textsuperscript{153}.

In line with this circumspect approach, it is apposite to realize that the exact nature of physical mechanisms governing observed optical AB oscillations are debated until today. For instance, AB oscillations were originally devised for instances when a Lorentz force is \textit{not} present but optical experiments usually consider oscillations of AB type assuming the magnetic field is concentrated in the middle of the quantum rings\textsuperscript{145}.

The question thus arises if incorporation of Lorentz force into the analysis for optical AB oscillations would serve to amplify them or result in alternate physics. The correct method of quantizing the magnetic vector potential coupling to the charged particle is also the subject of dispute as alternative methods signify different physical meanings\textsuperscript{154}. Other authors argue for quantifying the phase shift through determination of the changes in the de Broglie wavelength as it interacts with the magnetic vector potential, potentially leading to an altered view of what constitutes AB oscillations today\textsuperscript{155}. Experimental observation of AB oscillations in Type-II quantum rings nevertheless advances current research of complex quantum phenomena in novel semiconductor nanostructure systems.

In summary, the physical properties of 10 stacked layers of quantum rings have been investigated with photoluminescence and time-resolved photoluminescence techniques. Despite the large density of nanostructures in the ensembles, activation energies with temperature and typical Type-II behaviour with excitation power could be determined. Apart from this, the intricate physics governing extended carrier lifetimes and detection of quantum phase coherence are expected to advance research on this material system especially for applications related to memory and storage. The contribution of the wetting layer on the carrier dynamics of self-assembled nanostructures was also found to be significant. Finally, the optical properties were found to be consistent with that determined from single stack quantum rings, suggesting the scalability of the nanostructure system.
4. InGaAsN:H Quantum Dots

Novel methods of generating exceptionally sharp hydrogen diffusion profiles\textsuperscript{156} have enabled the innovation of dilute nitride nanostructures through spatially selective hydrogen irradiation at nanometer scale demarcations. Considering the extremely strong effect of dilute nitride on the bandgap of III-V semiconductors even at smaller concentrations\textsuperscript{157}, the ability of hydrogen irradiation to reverse them are valuable in the research of dilute nitride systems.

The complete nullification of nitrogen perturbation effects on the host lattice can be additionally achieved without corrugated sidewalls due to air exposure in much slower lithographic techniques and large fluctuations in material composition and morphology typical of structures grown via self-assembly\textsuperscript{158}. These superior attributes of hydrogen passivation present conspicuous advantages in propitiating the increasingly stringent requirements for spectral, spatial and electronic features in semiconductor nanostructures.

The efficacy of hydrogenation can generally be attributed to the small relative size and high electronegativity of N atoms which increase the electronic charge density around them, attracting the formation of H\textsuperscript{+} and N bonds. This ‘molecular orbital’ between H and N leads to a bonding level different from and lower in energy than that of the original N level, neutralising the electrical activity of nitrides through a decrease in the number of effective N atoms\textsuperscript{159}. 
Small scale modulation of the dilute nitride bandgap in the growth plane has consequently led to the nanofabrication of pyramidal quantum dots, site-controlled quantum dots, and a single quantum dot within a photonic crystal cavity. Analogously, the recent developments in imaging of the shape and strain in nanoscale hydrogenated structures and in processes to dissociate N-H complexes demonstrate measures of exerting further deterministic control on the hydrogenated dilute nitride nanostructures. Hydrogenated InGaAsN nanostructures thus present intriguing potential in the investigation for new material systems for futuristic nanophotonic applications.

The strong bowing in their bandgap which enables flexible lattice-matched growth on GaAs, coupled with their ability to emit at wavelengths in the coveted low loss telecommunication window (1330nm and 1550nm) even with minute incorporations of N, make them extremely attractive for telecommunications applications. The seamless assimilation of spatially selective hydrogen passivation techniques with the inherent desirability of InGaAsN nanostructures has also been previously established via optical characterisation of InGaAsN:H V-groove nanowires.

In this chapter, the complex emission dynamics of ensembles of InGaAsN:H quantum dots with diameters of 600nm have been determined with optical spectroscopy techniques. As the resonant defect level of nitrogen occurs within the conduction band of InGaAs, the fluctuation of nitride composition directly perturbs the conduction band minimum in dilute nitride semiconductor alloys. The multitude of localized states which are created at energies higher than the conduction band minimum consequently provide short-range traps for electrons.

Investigation of carrier dynamics in dilute nitride alloys with optical spectroscopy techniques such as PL and TRPL with dependent variables of laser pulse energies and temperature are thus expected to present a predilection of electron population toward

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§ Quantum dots are generally used to describe 0D structures. As such, with diameters of 600nm, it would be more accurate to label these structures ‘laterally interrupted quantum wells’. However, for the purpose of this work the term quantum dot will be used to maintain consistency with the growth and fabrication team, as an eventual reduction in diameters to create 0D nanostructures is anticipated.
these higher-level localized states. In superposition, fingerprints of the hydrogenation technique which instigated the formation of the quantum dots are anticipated in the emission dynamics.

In dilute nitride structures grown with epitaxial methods, evidence of population of electrons to higher level localized states in the conduction band minimum is commonly found through $i$) an S-shape of the peak position in temperature dependence PL $ii$) wavelength-dependent carrier lifetimes in TRPL experiments and $iii$) a blue shift of peak position with excitation power$^{171}$[and references therein]. In the following discussion, these will be related to recombination from the conduction band minimum states which are altered by the incorporation of nitrogen whereas the additional carrier dynamics dictated by the hydrogenation technique of quantum dot formation will be ascribed specifically to shallow tail states.

To create the structure, a 5nm thick In$_{0.21}$Ga$_{0.79}$As$_{0.975}$N$_{0.0025}$ quantum well capped by a 90 nm thick GaAs layer quantum well was first grown by MOCVD on a GaAs semi-insulating substrate at the University of Marburg. Following this, titanium dots with a diameter of 600nm were deposited by electron beam lithography on top of the capping layer in Sapienza University of Rome. Irradiation with hydrogen ions by means of a low-energy (100 eV) Kaufman source was done in Rome with an ion current density of 25 μA/cm$^2$, and sample temperature at 190 °C for the entire duration of the process. These conditions ensure a trap-limited diffusion with a hydrogen forefront of less than 5 nm/decade resulting in very sharp interfaces between the hydrogenated and H-free regions of the sample$^{156}$. 
Figure 4.1: a) Structure of sample before hydrogenation process b) 250s and c) 500s after hydrogenation [Picture courtesy of S. Younis]

Figure 4.2: Optical sample structure before and after hydrogenation leading to the formation of InGaAsN:H quantum dots
A biconvex lens with a focal length of 2cm was used for optical experiments, exciting approximately 25 quantum dots. The radius of the laser spot size and distance between the dots are shown in Figure 4.3. Time resolved streak images were obtained with low temperatures of 8K and excited confocally with the 690nm pulse produced by a Ti:Saph laser with a repetition rate of 80MHz (pg.34). As the laser pulse decay is 10ps, two orders of magnitude shorter than the quantum dot decay time (≈100ps to 600ps), the pulsed Ti:Saph laser could also be employed in PL measurements (available states can be filled in sufficient time before arrival of next laser pulse).

4.1 Laser energy pulse dependent TRPL

Figure 4.4 shows five vertically stacked streak camera images of the 600nm InGaAsN:H quantum dot ensemble with varying laser pulse energies per quantum dot. Each streak image maintains a vertical time axis of 2.2ns across the measured wavelength range 1200nm to 1300nm and Table 4.1 shows the calculation of energy per laser pulse per quantum dot from the applied average excitation power.
Table 4.1: Energy per laser pulse per quantum dot, $E_{\text{pulse}}/QD$ calculated from average excitation power over 25 InGaAsN:H quantum dots.

<table>
<thead>
<tr>
<th>Average excitation power, $P_{\text{exc}}$ (mW)</th>
<th>Energy per laser pulse, $E_{\text{pulse}}$ (pJ)</th>
<th>Energy per laser pulse per quantum dot, $E_{\text{pulse}}/QD$ (pJ)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$P_{\text{exc}}$ (mW) /80MHz</td>
<td>$E_{\text{pulse}}/25$</td>
</tr>
<tr>
<td>0.08</td>
<td>1</td>
<td>0.04</td>
</tr>
<tr>
<td>0.2</td>
<td>2.5</td>
<td>0.1</td>
</tr>
<tr>
<td>1</td>
<td>12.5</td>
<td>0.5</td>
</tr>
<tr>
<td>2</td>
<td>25</td>
<td>1</td>
</tr>
<tr>
<td>3</td>
<td>37.5</td>
<td>1.5</td>
</tr>
<tr>
<td>4</td>
<td>50</td>
<td>2</td>
</tr>
<tr>
<td>5</td>
<td>62.5</td>
<td>2.5</td>
</tr>
</tbody>
</table>

In all five images, an asymmetric shape of the emission toward longer wavelengths is evident. The emission that trails off the primary radiative recombination is characteristic of a density of states that extend into the bandgap much like a ‘tail’. These shallow tail states (STS) and the primary emission from states in the conduction band minimum (CBMS) are indicated in Figure 4.4. Collectively, STS and CBMS make up the lowest available energy for electron occupation usually referred to as the ground-state emission. In order to appreciate the contrast in relative intensity between the STS and CBMS emissions with increasing $E_{\text{pulse}}/QD$, post-experimental image processing was not applied to the streak images in Figure 4.4. As such, the $x$-axis shows emission wavelengths as they are measured in the streak camera (higher to lower photon energies from right to left in Figure 4.4).
Figure 4.4: Streak camera images of InGaAsN:H quantum dot ensemble with increasing laser pulse energies. The colour legend in the image represents the magnitude of relative intensity on the streak camera photocathode and the white diamonds correspond to peak emission.
The origin of STS can be traced to the hydrogen passivation of nitrogen in the quantum well surrounding the quantum dots. Notwithstanding the efficiency of N-$n$H $\geq 3$ (where $n$ is a positive integer, $n > 0$) complexes with $C_{1h}$ symmetry (also known as canted or asymmetric $C_{2v}$)$^{172,173}$ in reversing the effects of nitrogen perturbation in the dilute nitride lattice, N-$n$H $\leq 3$ complexes generally participate less effectively in this process$^{174}$. The preferential bonding of H to specific N complexes$^{175}$ also reduce the probability of passivating denser N pairs.

As a result, partially passivated N atoms catalyse the formation of shallow localization centres, energetically positioned below the quantum dot ground state$^{176}$ and extending into the InGaAsN energy gap. Due to the acceptor-like nature of N atoms that predominantly affect only the conduction band minimum as mentioned above (the valence band remains mostly unperturbed), only CBMS have been considered when optically characterising the ground-state emission of the InGaAsN:H quantum dot ensemble.

In the first streak image, similar electron occupancy at 0.5pJ/QD between STS and CBMS of the InGaAsN quantum dots create little discrepancy in their relative intensities. As $E_{\text{pulse}}$ /QD increments however, the higher density of states in the conduction band dominates the electron contribution to the overall emission and a progressive disparity in colour contrast between the STS and CBMS is noted from 1pJ/QD to 2.5pJ/QD. Additionally, a blue shift in peak wavelength (white diamonds) accompanies the simultaneous broadening of CBMS emission with increasing excitation powers.

In Figure 4.5, the decay curves extracted from all five streak images from 1205nm to 1275nm are plotted in energy scale (the 80nm range enables direct conversion with little effects despite the reciprocal nature between wavelength and energy). The decay times of emission from STS are at the lowest energies (first set of points in Figure 4.5) and from CBMS for all subsequent points.

With higher $E_{\text{pulse}}$/QD, the carrier lifetimes of STS emission can be observed to decrease as the influx of free carriers provokes an intensification of inelastic and elastic collision between carriers in the STS, providing them with the necessary kinetic energy.
Figure 4.5: Trend in carrier lifetime with $E_{\text{pulse/QD}}$ with solid lines representing fits from Equation 4.1. The mobility edge, $E_m$ increases in energy from 0.5pJ/QD to 2pJ/QD. The inset shows i) a pictorial representation of the carrier saturation mechanism in localized states with higher $E_{\text{pulse/QD}}$ (same colour representation as data points) and ii) (top right corner) electron dynamics at spectrum energies above and below the mobility edge. All drawings are considered in k-space.

to escape from their shallow states. On the other hand, the longer lifetimes extracted at the lower energy ranges diminish steadily at higher energies for the CBMS. This strong dependence of recombination lifetimes on energy at low temperatures are attributed to localized excitons\textsuperscript{177}. Here, strongly localized excitons at spectrum energies below a certain threshold contribute directly to radiative recombination and participate in a multitude of carrier transfers such as carrier cooling, intraband and phonon-assisted transitions at spectrum energies above this threshold. These non-radiative ‘exciton
hoppings’ occur at time scales too fast to be observed with measurement resolutions of 20ps. In this way, the observed radiative recombination at higher spectrum energies are a product of delocalized or localized excitons and can be easily transferred out of their sites\textsuperscript{178}.

Undulations in the ground state of the electrons (and holes)\textsuperscript{179} in systems with short range alloy disorder in the lattice nonetheless produce evidence of this resilient energy dispersive behaviour through a strong energy dependence in carrier lifetimes. In dilute nitride structures, the lack of preservation in the lattice crystalline nature is ascribed to the large difference between the size and mobility of N and host atoms, leading to the formation of N cluster aggregates during the growth process, and with it opportunities for multiple electron localization centres above and below the conduction band edge\textsuperscript{180,181}.

\textbf{Figure 4.6:} Decay curves at 2.5pJ/QD extracted every 10nm from 1200nm to 1270nm, with wavelength legend representing center wavelength. The decay curve of the STS emission at 1275nm is not shown.
Additionally, the mono-exponential nature of the decay curves signifying rapid depopulation of carriers from a single state of free carrier occupancy is depicted in Figure 4.6 for CBMS at $E_{\text{pulse}}/\text{QD}$ of 2.5pJ.

The CBMS fit of data points are subsequently fitted with Equation [4.1] to determine the energy threshold described above (hereafter referred to as the mobility edge$^{177}$, $E_m$) excluding the first point of the STS emission. Equation [4.1] thus follows as,

$$\tau(E) = \frac{\tau_R}{1 + e^{\frac{E-E_m}{\alpha}}}$$

[4.1]

where $\tau_R$ is the maximum decay time at each $E_{\text{pulse}}/\text{QD}$, $E_m$ is the mobility edge at which the recombination rate equals the transfer rate so that at $E<E_m$, excitons combine radiatively and $E>E_m$ facilitates multiple carrier transfer mechanisms, and $1/\alpha$ represents the model dependent energy-scaling factor, which has been used to describe exciton transfer rate between localized states in alloys$^{182}$. Although these processes are not directly deduced in this analysis, the values are presented for the purpose of comparison.

Here, it is noted that the term exciton was originally used (following the traditional definition of a bound electron-hole pair below the conduction band minimum (and valence band maximum) which partake in radiative recombination at low temperatures) to describe the carrier lifetime behaviour in alloy fluctuating GaAsP quantum wells$^{183}$, where the fluctuation in alloy composition of the ternary GaAsP precipitated the formation of localized energy states within the alloy. Since then, this phenomenological model has been used to describe systems with energy dependent carrier decay times characteristic of localized excitons in alloys with a variance in composition.

Although the density of localization centres prevalent in the conduction band minimum in dilute nitride structures do not preclude radiative recombination from multi-excitonic complexes, the term ‘exciton’ will be maintained here for consistency with literature.
From the table, the mobility edge, $E_m$ advances in energy from 0.995eV to 0.999eV with excitation pulse energies of 0.5pJ/QD to 2pJ/QD before reaching a saturation point, establishing that the average energy level of the ground-state becomes higher with greater free carrier densities.

**Table 4.2: Mobility edge, $E_m$ and scaling factor, $1/\alpha$ values obtained from fitting of data with Equation [4.1] (plotted in inset of Figure 4.7)**

<table>
<thead>
<tr>
<th>$E_{\text{pulse/QD}},$ (pJ)</th>
<th>Scaling factor, $1/\alpha$ (meV)</th>
<th>Mobility edge, $E_m$ (eV)</th>
<th>Maximum carrier lifetime, $\tau_R$ (ns)</th>
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<td>8.20</td>
<td>0.999</td>
<td>0.63</td>
</tr>
</tbody>
</table>

This is a direct consequence of the inclination of electrons to inhabit elevated localization centres in dilute nitrides and is commensurate with the increase in effective mass observed for electrons in the InGaAsN/GaAs conduction band\textsuperscript{184,185} and along with their low mobility as postulated by the Band Anticrossing Model\textsuperscript{186}. From excitation pulse energies of 0.5pJ/QD to 2pJ/QD, radiative recombination is thus dominated by electrons occupying successively higher energy localization states.

Extended recombination times in this excitation range subsequently ensue due to a steady augmentation of annihilating carriers with constricted overlaps from higher CBMS states. The filling of higher energy localized states is also characterized by a broadening of the emission toward the higher energy spectrum, further indicating radiative recombination between narrow wavefunctions of localized electrons and the more expansive wavefunctions of free holes\textsuperscript{187}.

After excitation pulse energies of 2pJ/QD however, the available localized energy states are categorically saturated and despite the proliferation in rate of recombination from CBMS (inset of Figure 4.8), the measured carrier lifetime values reach a plateau. Decay curves at 1245nm plotted for all laser pulse energies illustrate this in Figure 4.7.
Figure 4.7: Decay curves at 1245nm with increasing $E_{\text{pulse}}/QD$. The inset shows trends in the mobility edge, $E_m$ and scaling factor, $1/\alpha$.

There is thus a transfer in the principal mechanism underlying radiative recombination from STS at low excitation pulse energies $<0.5\text{pJ/QD}$ to CBMS at higher pulse energies $>1\text{pJ/QD}$ to $2.5\text{pJ/QD}$. This can also be seen from decay traces extracted at 1245nm for all $E_{\text{pulse}}/QD$ in Figure 4.7 where progressively longer decay traces from $0.5\text{pJ/QD}$ to $2\text{pJ/QD}$ and similar traces for $2\text{pJ/QD}$ and $2.5\text{pJ/QD}$ are observed. The inset depicting the mobility edge and scaling factor saturation further substantiate the plateau in rate of carrier transfer between localized states beyond $2\text{pJ/QD}$. Transient measurement techniques have thus allowed the identification of the exact energies of all radiative recombination channels in the InGaAsN:H quantum dot ensemble.

The discussion above is also illustrated pictorially in inset i) of Figure 4.5 above. Below $0.5\text{pJ/QD}$, carriers voluminously occupy the STS (shown as grey solid circles at the bottom of the drawing), before advancing to higher energy localized states with the
influx in free carrier density from 0.5pJ/QD to 2pJ/QD. At 2.5pJ/QD, all vacant higher level localized states are filled, and the gain in photoluminescence intensity is associated only to an increase in volume of recombining carriers.

4.2 Laser energy pulse dependent PL

Power dependent PL spectra from measurements done at 8K are shown in Figure 4.8 with an inset of the integrated intensity. The peak energy positions and FWHM of all the spectra are plotted in Figure 4.9. From Figure 4.8, an asymmetric PL lineshape with a tail extending to lower energies is apparent at low excitation powers 0.04pJ/QD, 0.1pJ/QD and 0.5pJ/QD. The disproportionate enhancement in luminescence at lower energies of the spectrum at these E_{\text{pulse}}/QD values is imputed to recombination originating from the STS and lower CBMS at relatively low excitation pulse energies. Although the integrated intensity amplifies at this range (first three points in inset Figure 4.8) the FWHM is not affected.

Considering that the superposition of STS and lower CBMS do not have a defined potential to determine electron occupancy, the static FWHM attests to the fluidity of carrier transfer between STS and lower CBMS. Significant blue shifts in the peak average energy positions with excitation pulse energies less than 0.5pJ/QD are nevertheless observed from Figure 4.9, establishing that the ubiquity of higher energy localized states in dilute nitride semiconductors easily encourages radiative recombination from them.

A sudden divergence in this trend is detected between 0.5pJ/QD and 1pJ/QD however, where the red shift in peak positions at 0.5pJ/QD accompanies a surge in FWHM broadening. This anomalous behaviour is the result of electrons in STS and lower CBMS competing vigorously with electrons in higher CBMS to contribute to radiative recombination.
Figure 4.8: Laser pulse energy dependent PL spectra of the InGaAsN:H quantum dot ensemble. The inset shows the semilogarithmic plot of integrated intensity with increasing $E_{\text{pulse}}/\text{QD}$.

Notwithstanding this, the incursion of free carriers primarily elicits radiative recombination only from higher CBMS beyond 1pJ/QD. This reversal in recombination dynamics incites a uniform increase in PL intensity at the higher energy region. In the second range marked in Figure 4.9, the FWHM broadens steadily, and is characteristic of many-particle Coulomb interaction effects, particularly in quantum dots with larger diameters.
Figure 4.9: Peak position and FWHM derived from Figure 4.8. Radiative recombination occurs primarily from shallow tail states (STS) below 0.5pJ/QD and from CBMS after Time-integrated PL experiments are thus able to provide an intriguing contrast in the complex carrier dynamics discerned from transient TRPL data (streak images between 0.5pJ/QD and 1pJ/QD in Figure 4.4 only evince a clear blue shift).

4.3 Temperature dependent TRPL

The five vertically stacked streak images in Figure 4.10 are obtained from time-resolved PL experiments done at temperatures of 8K to 100K at laser energy pulses of 1.5pJ/QD. From the normalized intensities (from post-experimental processing) between images, the emission of STS at longer wavelengths can be observed to disappear very quickly with increasing temperatures.
Figure 4.10: Temperature dependent streak camera images from 8K to 100K
The slight red shift at 75K spells the onset of significant thermal lattice expansion at 100K, at which point the bandgap reduction due to thermal lattice expansion and electron-phonon interaction (usually expected in semiconductors with applied thermal energy) governs carrier dynamics. Carrier lifetimes extracted at 10nm ranges from 1200nm to 1280nm are subsequently plotted in Figure 4.11 to evaluate the energy-dependent trend of the carriers with temperature variation.

Figure 4.11: Carrier lifetime trends with increasing temperatures. The inset shows carriers populating higher localized states up to 75K (light blue arrows), after which the surplus in kinetic energy propels them (dark blue arrows) to recombine from the conduction band minimum. The drawing is considered in k-space.

At 8K, carriers trapped in the STS have shorter decay times than CBMS carriers as seen in Figure 4.5 above. Carrier lifetimes at the lower energy end of the spectrum are
also protracted compared to the higher energy end, owing to the behaviour of localized excitons in alloys due to compositional fluctuations discussed above.

The higher energy trends in the CBMS continue at 25K, but electrons at the lowest CBMS that are lost to defects activated with small ionisation energies induce shorter lifetimes in the low energy region. Here, carriers in the STS emission can still be detected, although some have been able to escape their confinement.

With further increase of temperature to 50K however, the electrons gain the requisite thermal energy to completely desert the STS and populate localized energy levels situated higher in the conduction band. Carrier lifetimes at higher energies also become slightly longer here, as the electrons in elevated CBMS participate in additional carrier transfer activities in the aftermath of their acquired mobility.

Notwithstanding this continuing dynamic at 75K, thermally activated non-radiative recombination centres begin overpowering the luminescence output. Finally, at 100K, the electrons localized at higher energy levels in the CBMS possess adequate kinetic energy to plummet to the bottom of the conduction band. Thermal lattice expansion now presides over the recombination of carriers, and a red shift in peak energy position is observed in accordance with bandgap shrinking. The carrier migration and redistribution throughout this process contributes to the steady broadening of the FWHM seen in the streak images.
4.4 Temperature dependent PL

In Figure 4.12, the occupancy of electrons to higher level localized energy states due to kinetic energy accretion with temperature is evident from the blue shift in peak energy positions of the PL spectra from 8K to 75K. This behaviour is frequently encountered in the literature for nitride related structures with robust localization centres in the conduction band minimum\textsuperscript{190,191}. The extracted peak position and FWHM are plotted in the inset of Figure 4.13 along with the Arrhenius plot to determine the activation energy.

\textit{Figure 4.12: Temperature dependent PL spectra of the InGaAsN:H quantum dot ensemble}
The equation used for the fitting is described below,

\[ I = \frac{I_0}{1 + Ae^{(-E_A/k_BT)}} \]  

[4.2]

where \( I \) = measured photoluminescence intensity, \( I_0 \) = photoluminescence intensity at 0K, \( A \) = pre-exponential factors usually attributed to the rate of carrier recombination in crystalline semiconductors, \( k_B \) = Boltzmann constant in eV, \( T \) = finite temperature, \( E_A \) = activation energy of the thermally activated non-radiative recombination channel.

Figure 4.13: Arrhenius plot fitting of temperature dependent PL data. The inset shows peak position and FWHM behaviour with temperature increase.
The obtained value of 11.77meV, $k_B T = 136.6K$ ($A = 112$) for $E_A$ indicates that thermally activated non-radiative centres have a threshold of 136.6K. From Figure 4.12 however, it is ostensible that the quenching of luminescence takes place gradually, suggesting carrier traps with a range of ionisation energies and capture rate of free carriers exist in the system.

In essence, the InGaAsN:H/GaAs quantum dot ensemble is subject to a greater volume of passivation related lattice disorder in addition to the non-radiative channels of the InGaAs host matrix which directly impact their radiative recombination rates compared to InGaAsN:GaAs quantum wells. The quenching of luminescence for instance has been attributed to substitutional defects brought about by H binding to two or more N atoms and H induced rupture of bonds between N and host atoms. The N-H complexes involved in the hydrogenation process also accumulate compressive strain and lead to an expansion of the unit cell through stretched H cation-As bonds in the InGaAsN lattice, producing further lattice irregularities.

To recapitulate, the intricate carrier dynamics in the conduction band minimum of ensembles of 600nm InGaAsN:H quantum dots have been determined with varying $E_{\text{pulse}}/\text{QD}$ and temperatures.

The mobility edge, $E_m$ which increases with $E_{\text{pulse}}/\text{QD}$ from 0.5pJ/QD to 2pJ/QD before saturating at 2.5pJ/QD results in extended carrier lifetimes at the same pulse energy range. A transition in radiative recombination dynamics is also observed from laser pulse energy dependent PL spectra from energetically lower localized states to localized states at higher energies after a threshold of 0.5pJ/QD.

From 8K to 75K, the carrier dynamics are dictated by localization within the conduction band minimum. The onset of thermally activated defects leading to a gradual quenching of luminescence at 100K suggest that the inevitable gradient in the quantum dot periphery due to the chemistry of the passivation process creates substitutional impurities in its wake. The shallow states that trail off the conduction band edge of InGaAsN (a feature specific to the method of quantum dot formation) are thus in superposition to the deeper localization energy centres underlying the host lattice due to the incorporation of N.
Tremendous advances in semiconductor growth technology alongside percipience of III-Sb compound growth physics in recent years has elicited the fabrication of excellent quality complex Sb alloys such as Al$_{1-x}$Ga$_x$As$_{1-y}$Sb$_y$. The simultaneous tailoring of all four components of the quaternary stoichiometry enables fine tailoring of the bandgap for near-infrared operations, all while independent control of the lattice constant for lattice-matched growth on GaSb, InP and GaAs is maintained in parallel. MBE grown AlGaAsSb are thus extremely versatile, with applications ranging from barriers for mid-IR QW lasers and diode lasers, DBRs for VCSELs and as avalanche regions for APDs.

Al$_{0.85}$Ga$_{0.15}$As$_{0.56}$Sb$_{0.44}$ alloys have displayed high tolerance to temperature fluctuations as well as low noise characteristics as avalanche regions in APDs. Its high gain-bandwidth product also matches that of the AlAs$_{0.56}$Sb$_{0.44}$ avalanche region, lately reported as having the lowest excess noise to date in the 1550nm region. At this composition, the bandgap of Al$_{0.85}$Ga$_{0.15}$As$_{0.56}$Sb$_{0.44}$ is predicted to be indirect, such that the ground state radiative recombination occurs from the $X$-valley. Direct optical assessment of this indirect $X$-valley bandgap, $E_g^{X}$ is nonetheless unpublished.

Notwithstanding the limited susceptibility to thermodynamics of surface atomic bonding in MBE, the parameter growth window for III-AsSb systems is still inflexible due to the inherent complexities surrounding incorporation of Sb. For instance, the As-Sb exchange on the growth surface is highly dependent on temperature.
and the sticking coefficients of the Sb and As are not unitary as a consequence of the elements’ volatility\textsuperscript{215}.

Consequently, the growth of III-AsSb entails careful manoeuvring of total group-V flux and growth rate\textsuperscript{216} apart from controlling the As:Sb flux ratio and growth temperature. As a result, the ideal stoichiometry ratio could be affected (particularly in intricate quaternary composites), leading to segregation of Sb within the alloy. If bandedge transitions are ascertained by optical characterisation tools, the obtained spectral components could ultimately be traced to these growth kinetics.

In this chapter, PL data of the $E_g^X$ in Al$_{0.85}$Ga$_{0.15}$As$_{0.56}$Sb$_{0.44}$ is presented at low temperatures. Microsecond long carrier lifetimes have also been recorded at low temperatures with time-resolved PL experiments. The 500nm thick AlGaAsSb bulk layer was grown by MBE at the University of Sheffield on a semi-insulating InP layer with a 200nm InGaAs buffer layer (lattice matched to AlGaAsSb) deposited directly after the substrate. A 20nm thick InGaAs is grown as a capping layer after the quaternary alloy.

![Figure 5.1: Optical sample structure of Al$_{0.85}$Ga$_{0.15}$As$_{0.56}$Sb$_{0.44}$](image)
5.1 Temperature dependent PL

Figure 5.2 shows the intensity normalized temperature-dependent PL spectra of the AlGaAsSb bulk layer from 8K to 50K with an inset of integrated intensity at the same temperature range obtained with a 650nm Picoquant laser diode (pg. 33) with an average power of 0.4mW.

![Temperature dependent PL spectra](image)

*Figure 5.2: Temperature dependent PL spectra of the Al$_{0.85}$Ga$_{0.15}$As$_{0.56}$Sb$_{0.44}$ alloy with inset of integrated intensity of collective $x_1$ and $x_2$ peak*
The salient feature attributable to the AlGaAsSb alloy in the figure has two spectral components labelled $x_1$ and $x_2$. Here, the broader FWHM and lower relative intensity of $x_2$ is attributed to the energy potential of dissociated Sb during alloy growth as discussed above. As a consequence of quaternary growth kinetics, $x_2$ is also expected to be rife with localized defect states.

On the other hand, the features around 1.35eV are related to the InP substrate. As the luminescence of the collective AlGaAsSb peak disappears at 50K, a relative increase in intensity of the InP peak eventuates around 1.4eV. From the inset, a two order decrease in magnitude can also be observed in the overall AlGaAsSb spectral intensity from 8K to 50K.

![Figure 5.3: Trend in peak positions and FWHM with temperature. The k-space depiction of the alloy bandstructure in its ground state is drawn in the inset with energy values obtained from PL and calculations from University of Sheffield](image)

Figure 5.3: Trend in peak positions and FWHM with temperature. The k-space depiction of the alloy bandstructure in its ground state is drawn in the inset with energy values obtained from PL and calculations from University of Sheffield.
In Figure 5.3, the aggregate peak position and FWHM of the AlGaAsSb peak from PL spectra in Figure 5.2 are plotted. The two spectral components could not be separated or fit reliably with Gaussian functions, suggesting that there is no distinct allocation of $x_1$ and $x_2$ states within the energy gap. Nevertheless, the average value of the two components enables determining a 20meV reduction in the bandgap from 8K to 50K. A 13meV broadening of the FWHM additionally outlines the range of carrier redistribution energies in the indirect bandgap with temperature increase.

A schematic illustrating the bandstructure of the AlGaAsSb alloy with the indirect bandgap value established by PL is also drawn in the inset of Figure 5.3. Previous spectral response measurements in Al$_{0.85}$Ga$_{0.15}$As$_{0.56}$Sb$_{0.44}$ alloys have enabled the estimation of the direct and indirect bandgap values of 1.77eV and 1.56eV respectively through linear extrapolations$^{209}$.

The curtailment from 1.560eV to 1.547eV in the experimentally measured indirect bandgap is attributed to $i$) the spectral component, $x_2$ which effectively lowers the average ground state energy of $E_g^X$ and $ii$) to the likely presence of impurity bound states at the bandedges due to native defects such as Ga vacancies and Sb$_{Ga}$ antisites.

An enhancement of photoluminescence intensity at low temperatures in bulk indirect semiconductors can occur due to recombination from free excitons$^{217,218}$ as additional $e-h$ pairs are created for phonon-assisted radiative recombination with slight increase in temperature. Even if free exciton recombination cannot be detected, the photoluminescence intensity at cryogenic temperatures remain relatively constant in indirect semiconductors such as Sr$^{219,220,221}$, In$_2$O$_3$$^{222}$, TlBr$^{223}$ etc. The photoluminescence intensity in the AlGaAsSb alloy nevertheless undergoes complete quenching at 50K.

This phenomena is observed in indirect bandgap GaAs$^{78}$ and SiGe$^{224,225}$ alloys with disorder and is the direct result of fluctuations in the bandedges which create traps for the recombining $e-h$ pairs. As the charge carriers here are subject to localization below a certain energetic ‘mobility edge’, annihilation of carriers occurs through non-radiative recombination even with acquisition of low levels of thermal energy. Considering the complexities of AlGaAsSb growth outlined above and the separation of the spectral components, this is a likely scenario. In order to verify this further, excitation power
dependent PL experiments could be done to determine the trends of electron occupancy in the bandstructure. Temperature-dependent PL experiments could also be done with a shorter interval between the data points (such as 2K) at the lower energy region to analyse the peak position behaviour. Additionally, a more extensive calculation of the band parameters of AlGaAsSb with varying Ga composition could give a comprehensive picture of the bandprofile and nearby carrier migration channels.

5.2 Temperature dependent TRPL

Time-resolved PL experiments were done from 8K to 30K with the same 650nm excitation source, now converted into low frequency pulses of 100kHz (pulse energy of 0.4nJ).

Streak camera images evincing carrier decay times in the indirect AlGaAsSb bandgap at 8K and 25K are shown in Figure 5.4. In order to improve the signal to noise ratio due to a rapid quenching of PL intensity seen above in Figure 5.2, images were obtained using a photon counting method described in pg. 29, with an acquisition time of 4 hours at each temperature. As post-experimental image processing techniques were not applied to demonstrate the exact relative intensities between the two images, the wavelength scale is reversed in the x-axis as higher energy photons are measured first in the streak camera.

A time window of 10µs was necessary to acquire both images, and the 20nm range used to extract decay times of the two spectral components $x_1$ (PL peak position at 800nm) and $x_2$ (PL peak position at 820nm) are indicated. At 8K, the signal to noise ratio is high, and the emission is narrow and extended. By 25K however, the signal to noise ratio has degraded considerably and a contrasting behaviour in the emission can be qualitatively distinguished. After 30K, the decay curves could not be extracted anymore despite the long acquisition time.
Figure 5.4: Streak images of $Al_{0.85}Ga_{0.15}As_{0.56}Sb_{0.44}$ bulk at 8K and 25K. The colour legend indicates the relative intensity of the photons impinging the photocathode.
Monoexponential decay traces for $x_1$ from 8K to 30K in Figure 5.5 demonstrate the progressive truncation of the indirect radiative recombination channel with temperature. The single decay channel implies that radiative recombination occurs only from $E_g^{x}$ without substantial carrier migration between the spectral components at the measured temperature range.

![Graph showing monoexponential decay curves from 8K to 30K for $x_1$.](image)

Figure 5.5: Monoexponential decay curves from 8K to 30K measured for $x_1$

Decay times from fitting with single exponential decay functions for $x_1$ and $x_2$ from 8K to 30K are subsequently plotted in Figure 5.6. The initial carrier lifetimes recorded at $\leq 3.5\mu s$ at 8K abate significantly after 16K to $\approx 1\mu s$ at 30K. Microsecond long decay times are consistent with those observed for indirect bandgaps in other bulk semiconductor systems\textsuperscript{226,227,228}. The long decay time of the indirect bandgap thus denotes good crystalline quality in the material grown.
In addition, the carrier lifetimes of $x_2$ are consistently longer than $x_1$ throughout the experiment. As $x_2$ states are anticipated to be dominated by Sb clusters, their extended decay times are related to radiative recombination from localized defect states. The inset of the figure exhibits this difference in the decay curves of $x_1$ and $x_2$ at 25K (the laser pulse used to trigger carrier decay is included for comparison).

![Figure 5.6: Plot of carrier lifetime of the two spectral components. The inset shows the decay curves of $x_1$ and $x_2$ at 25K alongside the laser pulse decay measured in the same time window for comparison.](image)

In conclusion, the optical properties in bulk Al$_{0.85}$Ga$_{0.15}$As$_{0.56}$Sb$_{0.44}$ alloy have been evaluated from 8K to 50K. At the low temperatures measured, two spectral components are observed in the indirect bandgap and are attributed to a diversity in the quaternary alloy composition. The complete quenching of luminescence intensity at 50K is related to a possible carrier transfer after 50K to the nearby $\Gamma$-valley.
Monoexponential decay times of the order of microseconds signifying single radiative recombination channels from the $E_g^X$ valley have also been ascertained up to 30K. Customisation of the composition of Al and Sb has thus resulted in an indirect bandgap detectable by optical spectroscopy methods. The data communicated above substantiates the growth flexibility of the quaternary AlGaAsSb alloy material and its ensuing potential for precise bandgap engineering.
6. Conclusion

In this thesis, three different and novel III-V semiconductor systems have been evaluated with photoluminescence spectroscopy techniques. The optical properties obtained from each experiment is outlined below, followed by a general summary and suggestions for future work. Finally, a feedback to the PROMIS-ITN relating to the growth and applications of the semiconductor structure is discussed.

1. GaSb/GaAs quantum rings
   - Temperature-dependent PL
     Activation energies of defects and localized defect states of the quantum ring ensemble and wetting layer which facilitates carrier escape after 75K were determined. Similar physical trends were observed in both the 10 layer and 1 layer sample.
   - Excitation power-dependent PL
     Type-II behaviour was observed from the strong blue shift in peak position with increasing free carrier density in addition to the exact mechanism behind different power law trends in the peak position shift in the low and high excitation regimes. Similar physical trends were observed in both the 10 layer and 1 layer sample.
   - Temperature-dependent TRPL
     Duality in trends of radiative and non-radiative carrier lifetimes were detected from the decay trends where the radiative lifetime increase was attributed to the annularity of the quantum rings. Further, the extended carrier lifetime values were related to i) Type-II band alignment ii) ring-shape of the nanostructures which reduces the electron-hole wavefunction overlap, prolonging the instance of radiative recombination and iii) the low excitation power density used which causes free e-h
pairs to be quickly depleted. Similar physical trends were observed in both the 10 layer and 1 layer sample.

- **Magnetic flux density-dependent PL**
  Quantum coherence was established from the detection of Aharonov-Bohm oscillations in the quantum ring peak energy positions for the 10 layer quantum ring structure. A difference in the oscillation period was also observed when increasing the excitation power by one order of magnitude and ascribed to the band bending effect in the quantum rings at the high excitation regime. Additionally, a correlation in the intensity profile of the quantum ring and the wetting layer was detected at the higher excitation power used and related also to the band bending of the Type-II heterojunction deduced from excitation power dependent PL experiments.

*Summary & future work*: The scalability of carrier dynamics to a single layer of quantum rings could be extended to a single quantum ring. This would require specialised growth techniques to enable site-controlled rings while still maintaining the capping method used for their formation. Optical characterisation would involve a micro-PL setup with an objective lens, and the sample would be mounted on a vibration-resistant cryostat for PL and TRPL experiments under similar excitation conditions. The development of these site-controlled growth techniques in the Type-II quantum rings would also allow for the development of applications such as spin-dependent electrostatic gating with the extended carrier lifetimes facilitating their tunability.

*PROMIS-ITN feedback*: The cold-capping method is effective in producing stacked layers of quantum rings as long as a certain thickness of spacing layer is maintained. If more stacks are to be grown, the MBE growth recipe must be modified since the reduction in temperature necessitates more atomic layers of GaAs to compensate for the strain-related defects in the 7.8% lattice mismatch. Further, methods to minimise the localized defect states brought about by composition fluctuation in the quantum rings could be implemented. However, as far as intermediate band solar cells are concerned, there is definitely a clear peak around the expected energy value of the GaSb/GaAs nanostructures which indicate that this layer could absorb longer wavelengths to increase the spectral response of the solar cell.
2. InGaAsN:H quantum dots

- Laser pulse energy-dependent TRPL
  A strong wavelength-dependent carrier lifetime was found in the conduction band minimum states and attributed to recombination from localized excitons in alloys with an inherent disorder due to a fluctuation in composition. Traces of the hydrogenation method of quantum dot could also be detected from shallow tail states that trail off the edge of the conduction band minimum.

- Laser pulse energy-dependent PL
  The trends of the PL lineshape show that the source of carriers that contribute to radiative recombination shift from the shallow tail states to the conduction band minimum states.

- Temperature dependent-TRPL
  Up to 75K, the wavelength dependent carrier lifetime can still be observed, and carrier dynamics are influenced by the localized states in the conduction band minimum. At 100K, the wavelength-dependent behaviour disappears completely, and the carrier lifetime values are almost constant throughout the spectra. The shallow tail states also desert their occupancy at 50K.

- Temperature dependent-PL
  The carrier dynamics are dictated by the localized states before 75K, leading to a blue shift in PL and a red shift after 75K. The activation energy of defects could also be found from the intensity profile.

Summary & future work: The carrier dynamics in the quantum dots are a superposition of the localized states in the CBMS ubiquitous in dilute nitride structures and the STS particular to the hydrogenation that precedes their formation. Autocorrelation could be done on the quantum dots to establish their suitability as single photon sources. This would require samples grown with a means of determining their exact location under the mask. With sufficient signal collection, the PL and TRPL experiments in Chapter 4 could be done on quantum dots with smaller diameters to compare their physical properties.

PROMIS-ITN feedback: The participation of the STS in the recombination dynamics of these structures could present additional challenges in the actualisation of
hydrogenated dilute nitride nanostructure devices. This could potentially limit their functional dimensions and must be mitigated by tailoring fabrication techniques. Further, the strong wavelength-dependent carrier lifetime of the dilute nitride quantum dots which establishes strong electron localization in dilute nitride alloys must be taken into consideration if effective single photon sources are to be manufactured.

3. **Al$_{0.85}$Ga$_{0.15}$As$_{0.56}$Sb$_{0.44}$ alloy**
   - Temperature dependent PL
   Two spectral components as a result of quaternary alloy growth kinetics could be determined and attributed to the dissociation of Sb. There is a complete quenching of photoluminescence intensity at 50K related to the disorder in the alloy which promotes radiative recombination from localized electron-hole pairs.
   - Temperature dependent TRPL
   Microsecond long radiative recombination establishing luminescence from indirect $E^X_g$ valley. The decay curves are also monoexponential suggesting little to no carrier transfer between the spectral components

**Summary & future work:** The identification of two spectral components in the PL spectra attests to the difficulty of AlGaAsSb alloy growth. In order to verify the disordered nature of the quaternary alloy, excitation power-dependent experiments should be conducted at low temperatures to obtain any trends in the PL lineshape (asymmetry, peak position shift etc). Additionally, an increase of the number of data points in the cryogenic temperature region would be critical in providing a more thorough analysis of the nature of exciton localization in the alloy.

**PROMIS-ITN feedback:** It is essential to characterise optical samples without multiple layers having varying doping concentrations although this may be favoured by the growth team for cost-effectiveness. The indirect nature of the bandgap and long carrier lifetimes for instance, could not be detected in previous AlGaAsSb samples despite similar optical characterisation configurations. In addition, the FWHM of the quaternary PL peak can be narrowed by improving the growth recipe
to overcome the division of the spectral components. This could be a laborious pursuit however, in view of the complexities of III-V Sb growth discussed above. If the composition of Al and Sb in the quaternary alloy are varied in a range, the exact crossover point from Γ valley to the X valley can be determined with low temperature TRPL experiments and modulation spectroscopy techniques. Further, the alloy could be incorporated into a cryogenically cooled Single Photon Avalanche Photodiode (SPAD) or photomultiplier for electrical characterisation.
Appendix

A1. The standard lock-in technique

In luminescence spectroscopy of semiconductors, a method of measuring frequency-selective AC signals dubbed ‘the standard lock-in technique’ is commonly employed. As its name suggests, the technique involves a lock-in amplifier, a device primarily used to detect narrow bandwidth signals with very low amplitudes, thus requiring instrumentation that allows filtering of select wavelengths while also maintaining low noise figures so that high enough dynamic reserves can be achieved.

The working principle of the SR830 Stanford Research Systems dual phase lock-in amplifier is described analogously to phase synchronous detection. An emission from the sample, which is the signal of interest, $V_{lum}$ arrives at the lock-in at a set external frequency. This frequency is seen by the lock-in as the experiment reference frequency, $\omega_{Er}$ and it is supplied separately to the lock in throughout the experiment. The frequency at which the signal is detected by the lock-in therefore matches the frequency of excitation (modulating frequency not photon wavelength).

For all PL experiments in this thesis, the external reference frequency, $\omega_{Er}$ was provided by mechanical chopping of the excitation beam with an optical chopper at low frequencies $f \approx 150$Hz. The frequency of the chopper is controlled by a Stanford Research Systems SR450 chopper controller. A schematic of a basic signal detection setup with the standard lock-in technique used is shown in Figure A1.1 below.
Figure A1.1: The standard lock-in technique

Once received by the lock-in, a second reference sine wave produced by the lock-in’s internal oscillator, \( V_{Lr} \), locks to \( \omega_{Er} \) via a phase-locked loop (PLL), so that the frequency of \( V_{Lr} \) is now \( \omega_{Er} = \omega_{Lr} \). The phase of \( V_{lum} \) will be with reference to the externally supplied reference frequency \( \omega_{Er} \) denoted here as \( \theta_{Er} \), however the phase of \( \omega_{Lr} \) will be shifted from the value computed through the PLL by multiplication with a sine wave in the phase shifter so that the lock-in reference phase, \( \theta_{Lr} \) is independent of the reference frequency. This active tracking ensures that changes to \( \omega_{Er} \) will not affect the output measurement\(^{229}\).

\[
V_{Lum} \sin(\omega_{Er} + \theta_{Er}) \quad \text{and} \quad V_{Lr} \sin(\omega_{Lr} + \theta_{Lr})
\]

are then multiplied by the digital phase sensitive detectors (PSD) in the SR830 illustrated below in Figure A1.2. With digital technology, the splitting of the signal in dual-phase demodulation can be attained without losses in SNR, in addition to reducing errors as a result of mismatch in signal pathways, cross-talk and drifts\(^{230}\). The digital PSD also enables dynamic reserves of 100dB to be achieved (dynamic reserve being the ratio of the maximum signal that can be measured above the tolerated input noise level).

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Figure A1.2: Simplified block diagram of the SR830 lock-in amplifier. Both PSDs are digital and the instant at which each term in the signal multiplication of PSD1 is acquired in the process flow is indicated.

In PSD1, both the signals described above are multiplied leading to two AC signals containing the difference and sum frequencies of \( \omega_{Er} \) and \( \omega_{Lr} \).

\[
V_{PSD1} = V_{Lum} V_{Lr} \sin (\omega_{Er} t + \theta_{Er}) \sin(\omega_{Lr} t + \theta_{Lr})
\]

\[
= \frac{1}{2} V_{Lum} V_{Lr} \cos \left( [\omega_{Er} - \omega_{Lr}] t + \theta_{Er} - \theta_{Lr} \right) - \frac{1}{2} V_{Lum} V_{Lr} \cos \left( [\omega_{Er} + \omega_{Lr}] t + \theta_{Er} + \theta_{Lr} \right)
\]

When \( \omega_{Er} \neq \omega_{Lr} \), no output ensues after the low pass filter, as a suitably long time constant filters out low frequency AC signals and \((\omega_{Er} + \omega_{Lr})\) and \((\omega_{Er} - \omega_{Lr})\) are not expected to be within the low pass filter bandwidth. However, a DC signal proportional in amplitude to the input signal is produced when \( \omega_{Er} = \omega_{Lr} \) as \( \cos 0 = 1 \). The DC component output of the phase sensitive detector when \( \omega_{Er} = \omega_{Lr} \) is expressed below.

\[
V_{PSD1} = \frac{1}{2} V_{Lum} V_{Lr} \cos(\theta_{Er} - \theta_{Lr})
\]
In Figure A1.3, the output of $V_{\text{Lum}}$ and $V_{Lr}$ with $\omega_{Er} \neq \omega_{Lr}$ and $\omega_{Er} = \omega_{Lr}$ is demonstrated. On the left, the differing frequencies result in a sine wave with mixed $\left(\omega_{Er} + \omega_{Lr}\right)$ and $\left(\omega_{Er} - \omega_{Lr}\right)$ components, leading to a zero DC output after low pass filtering. When the frequencies are the same as shown in the right, the output before filtering is a single frequency sine wave with a fixed offset which produces a DC signal at the offset value after filtering.

Notwithstanding the successful detection of $V_{\text{Lum}}$, the phase dependency of the signal results in zero amplitude if the phase shift between the signals $\cos \left(\theta_{Er} - \theta_{Lr}\right) = 90^\circ$. In order to eliminate this phase dependency, a second phase sensitive detector $V_{\text{PSD}_2}$ is used to multiply the reference signal, $V_{Lr}$ with a $90^\circ$ phase shift so that the product $V_{\text{Lum}} \sin(\omega_{Er} + \theta_{Er})$ and $V_{Lr} \sin(\omega_{Lr} + \theta_{Lr} + 90^\circ)$ are computed. This creates a signal proportional to the $\sin$ after the low pass filter,

$$V_{\text{PSD}_2} = \frac{1}{2} \ V_{\text{Lum}}V_{Lr} \sin \left(\theta_{Er} - \theta_{Lr}\right)$$

*Figure A1.3: Signal filtering process for $\omega_{Er} \neq \omega_{Lr}$ and $\omega_{Er} = \omega_{Lr}$ shown from left to right. Note that phase differences which are also compensated with the dual phase lock-in amplifier have been omitted for simplicity.*
Phasor analysis is subsequently done on the two separate signals so that 4 main outputs of the lock-in amplifier, $X$, $Y$, $R$ and $\Phi$ are identified where,

$$X \approx V_{\text{Lum}} \cos \theta$$

$$Y \approx V_{\text{Lum}} \sin \theta$$

$$R = V_{\text{Lum}} = \sqrt{X^2 + Y^2}$$

$$\Phi = \tan^{-1} \left( \frac{Y}{X} \right)$$

For the experiments conducted in this thesis, the $R$ value is sent to the Labview software for readout of the signal. Apart from selecting suitable values of the time constant ($10\mu s$ to $3 \times 10^4 s$ at a reference frequency of $< 200Hz$), the sensitivity values ($2nV$ to $1V$) should be adequately monitored as it directly affects the resolution of the acquired PL spectra.
A2. Detector responsivity curve

Figure A2.1: Responsivity of New Focus 2151 Si and 2153 InGaAs femtowatt photoreceivers (picture adapted from product manual)
A3. Streak camera responsivity curve

Figure A3.1: Streak camera sensitivity plot (picture adapted from product manual)
A4. Signal dispersion

A Bruker Optics monochromator was employed to disperse the obtained luminescence from all PL experiments for signal analysis. In the Chromex 500sm scanning monochromator, three ruled grating options are available mounted on a turret table, 500/600, 150/1250 and 1200/1. As the emission signals considered in this work are in the near IR range and do not have very narrow linewidths, the 150/1250 grating was primarily used for PL spectra acquisition.

The Czerny-Turner configuration of the monochromator is shown below in Figure A3.1. Separate mirrors for collimation and focusing accommodates a flexible geometry of the optics. In the Bruker Optics model, toroidal mirrors are additionally used to compensate for astigmatism whereas wavelength scanning is done by means of a direct digital stepper-motor drive.

![Czerny-Turner configuration](image)

*Figure A3.1: Czerny-Turner configuration. Note that this picture represents a multichannel detector at the output in a spectrograph for illustration purposes (picture from Zemax simulation)*

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Monochromators are generally characterized by their dispersion, resolving power and throughput. Both angular and linear dispersion quantify the difference in wavelength between the measured value and a divergence as a result of the physical parameters of the optics.

Angular dispersion can be defined as the angle at which the light rays leave the dispersion element,

$$ A_D = \frac{\delta \theta}{\delta \lambda} \text{ rad/nm} $$

where $\delta \theta =$ angle variation in radians and $\delta \lambda =$ wavelength variation in nanometers

The focal length $f$, determines the spatial separation $\delta l$, with which two spectral lines $\lambda$ and $\lambda + \delta \lambda$ can be resolved. From this, it can be written that,

$$ \delta l = f \delta \theta $$

so that the linear dispersion can be defined as,

$$ L_D = \frac{\delta l}{\delta \lambda} \text{ nm} $$

In general, the reciprocal linear dispersion is more frequently used.

$$ L_D^{-1} = \frac{\delta \lambda}{\delta l} = \frac{1}{f} \frac{\delta \lambda}{\delta l} = \frac{1}{f A_D} \text{ nm/mm} $$

The value $L_D^{-1}$ is crucial because the spectral bandwidth, $\Delta \lambda$ of the instrument can be determined directly from the slit width, $\Delta s$ set during the experiment, as

$$ \Delta \lambda = L_D^{-1} \times \Delta s $$

Ordinarily, the exit and entrance slit width values are kept constant to facilitate spectral correction.

Although the dispersion of the grating is independent of its size\textsuperscript{23}, the resolving power, $R$ is strongly dependent on the size of the dispersion element. In accordance with the principle of light diffraction, significant broadening of the spectral lines can be
anticipated at the exit slit if grating with small effective area is used. Diameters of optical elements in the monochromator must thus be sufficient, and angle of collimation to the monochromator input properly aligned.

The resolving power $R = \frac{\lambda}{\Delta \lambda}$ of the monochromator is additionally dependent on many factors such as the illuminated width of the grating, grating order, groove density, angular dispersion, $A_D$, focal length, $f$ of the monochromator and slit width used in the experiment. A diagram illustrating the Rayleigh criterion of resolving peaks in monochromators with different focal lengths is shown in Figure A3.2. With longer $f$ values, spectral features that are juxtaposed can be separately distinguished although $d\theta$ values are shared between both devices.

![Diagram of resolving power in monochromators having different focal lengths](image)

*Figure A3.2: Resolving power in monochromators having different focal lengths*

Slit widths that are too small nevertheless result in a pronounced degradation of the signal to noise ratio and increases stray light in the monochromator. The optimum slit width value should therefore be maintained according to the approximation where the diffraction angle matches the geometric parameters of the device.
This relation can be written as,

$$\Delta s_{opt} \approx \frac{2f\lambda}{W}$$

where $f = \text{the focal length of the monochromator and } W = \text{the width of the diffraction grating}$

Other factors that may also result in reduced resolution are optical aberrations and parasitic reflections.

There are many terminologies used to quantify the radiant flux accepted and emitted by a light collecting system. This includes luminosity, throughput, entendue and aperture ratio\textsuperscript{232}. Despite the unstandardized approach, these definitions all attempt to express the efficiency of admitted light to achieve high signal to noise ratios. Although there are also myriad ways of defining this quantity, a throughput value with common experimental approximations will be used, and finally related to the resolving power discussed above.

The emitted radiant flux, $\Delta \zeta_i$ of an object can be written as,

$$\Delta \zeta_i = \Delta E \cos \Theta \Delta \Omega B$$

where $\Delta E = \text{emission area of the object, } \Theta = \text{angle between direction of radiation and normal to } \Delta E, \Omega = \text{magnitude of the solid angle of the radiation and } B = \text{a constant representing the brightness of the emission}$

This equation can be simplified based on experimental approximations to,

$$\zeta_i \approx E \left( \frac{W^2}{f^2} \right) B$$

where $\Delta E \rightarrow E$ is based on uniform iridescence across the monochromator entrance slit, $\Theta \approx 0$ due to the narrow collimation field of view and $\Delta \Omega \approx \frac{W^2}{f^2}$ based on the aperture ratio approximation.
If an additional term is included to account for the efficiency of the monochromator optics, $\chi$ where $\chi < 1$, the output flux, $\zeta_\lambda$ (the subscript $\lambda$ denotes the wavelength dependence of the output flux) is written,

$$\zeta_\lambda = \zeta_\iota \chi$$
The monochromator throughput is thus,

\[ \mathcal{T} = \frac{\zeta_\lambda}{B} \]

From this,

\[ \mathcal{T} = \chi E \left( \frac{W^2}{f^2} \right) \approx \chi E \left( \frac{A}{f^2} \right) \]

where \( A = \) area of the diffraction grating.

The throughput of spectral devices is commonly given in terms of an aperture ratio form \( \frac{f}{#} \), where \( # = \frac{f}{w} \). Larger values of \# signify lower throughput of the device.

Considering that it would be useful to have a relation between the resolution and output flux and throughput of the monochromator, \( E \) is redefined separately with respect to the width, \( w \) and height, \( h \) of the monochromator so that,

\[ E = wh \]

and

\[ \alpha = \frac{w}{f}, \quad \beta = \frac{h}{f} \]

where \( f \) is the focal length of the device. Now,

\[ \zeta_\lambda = \chi \alpha \beta W^2 B \]

and the spectral bandwidth defined above can be written as,

\[ \Delta \lambda = L_D^{-1} w \]

\[ = \frac{1}{f A_D} w \]

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As $= \frac{w}{f}$,

$$\Delta \lambda = \frac{\alpha}{A_D}, \quad \alpha = \Delta \lambda A_D$$

Since the brightness, $B$ is spectrally integrated across the monochromator entrance slit,

$$B = \int B_\lambda \, d\lambda$$

The value of $B$ can be substituted into the equation as $B_\lambda \Delta \lambda$ so that the output flux now reads,

$$\zeta_\lambda = \chi \beta W^2 \Delta \lambda^2 A_D B_\lambda$$

From the definition of resolving power, $R$,

$$R = \frac{\lambda}{\Delta \lambda}$$

Substituting the reciprocal of $R^2$ gives,

$$\zeta_\lambda = \frac{\chi \beta W^2 \lambda^2 A_D B_\lambda}{R^2}$$

clearly demonstrating that the output flux scales quadratically as a function of resolution.

In order to derive a relation with the throughput, $T$, the brightness is considered as $B$ instead of $B_\lambda \Delta \lambda$ as the difference in spectral integration of the input and output cancels out. The output flux is now,

$$\zeta_\lambda = \frac{\chi \beta W^2 \Delta \lambda A_D B}{R}$$

It follows directly that the throughput can be modified to,

$$R = \frac{\chi \beta W^2 \lambda A_D}{T}$$
From the discussion above, it can be directly inferred that the resolution is inversely proportional to the throughput if the slit height is considered uniform. The resolving power in a monochromator is also dependent on the angular dispersion and scales with the wavelength being dispersed. However, care must be taken to ensure that the slit width is not set too narrow, as diffraction of light at the monochromator entrance slit will occur.

In Table A3.1 below, a comparison of specifications between the same Chromex Bruker Optics scanning monochromator models with focal lengths 250mm and 500mm is shown to summarize the preceding discussion.

Table A3.1: Comparison of specifications of Chromex Bruker Optics scanning monochromator with different focal lengths

<table>
<thead>
<tr>
<th>Specification</th>
<th>250sm</th>
<th>500sm</th>
</tr>
</thead>
<tbody>
<tr>
<td>Focal length, $f$</td>
<td>250mm</td>
<td>500mm</td>
</tr>
<tr>
<td>Aperture ratio, $f/#$</td>
<td>$f/4.0$</td>
<td>$f/8.0$</td>
</tr>
<tr>
<td>Reciprocal linear dispersion, $L_D^{-1}$</td>
<td>3nm/mm</td>
<td>1.6nm/mm</td>
</tr>
<tr>
<td>Resolution, $R$ (FWHM)</td>
<td>0.15nm</td>
<td>0.07nm</td>
</tr>
</tbody>
</table>
A5. Jacobian conversion

Although the raw data of photon dispersion from the monochromator is recorded in wavelength, conversion of data from wavelength to energy is often vital to facilitate fitting with mathematical models. In this case, simple conversion of the intensity value to energy value using the relation $E = \frac{hc}{\lambda}$ is insufficient. As the relationship between wavelength and energy is reciprocal, the intervals $d\lambda$ are not equally spaced across the energy spectrum. If conservation of energy between the energy and wavelength intervals are applied,

$$f(E)dE = f(\lambda)d\lambda$$

Substituting Planck’s formula above it follows directly that,

$$f(E) = f(\lambda)\frac{d\lambda}{dE}$$

$$= f(\lambda)\frac{d}{dE}\left(\frac{hc}{E}\right)$$

$$= -f(\lambda)\frac{hc}{E^2}$$

The negative value denotes the direction of integration and can be omitted from the conversion.

Thus, in addition to scaling the photon energy values, the signal intensity itself must be scaled by $(hc/E^2)$. This correction is known as the Jacobian conversion\textsuperscript{233}. The multiplication enhances the spectrum at longer wavelengths, causing a red shift of spectral peaks. This effect becomes more pronounced the broader the spectra and is negligible if FWHM is few tens of nanometers.
A6. Closed-cycle He system for low temperature measurements

PL measurements are routinely done at low temperatures to ascertain the carrier dynamics of the system with minimal thermal perturbations. This enables comparison if further experiments are done at higher temperatures, allowing the effects of applied temperature to be identified. In this work, all low temperature measurements are conducted employing a closed cycle Helium cryostat which operates from 8K to 350K.

In a closed cycle system, the cryogen used to cool the cold end can be recycled back into the system with the use of a compressor. The cryogen is stored in specialised dewars and typically do not need to be changed for a few years. A schematic of the system with the Advanced Research Systems ARS4HW compressor is shown in Figure A5.1.

![Figure A5.1: Schematic of closed cycle He system (picture adapted from product manual) The cooling water is provided by the ARS4HW Coolpac unit](image-url)
Cold temperatures near the boiling point of He are achieved with a Gifford McMahon (GM) regenerative refrigeration cycle. Notwithstanding their serious power and heat dissipation requirements, the mature technology of air conditioning supports cost reduction in GM systems. Compared to the Stirling cycle for instance, the hermetically-sealed GM compressor operates in DC mode with the AC flow being supplied separately by the rotating valves that alternate pressure flow in the expander between hotter high pressure and cooler low pressures.

This possibility of decoupling the coldhead from the compressor is a definite advantage of GM cryocoolers. Longer machine lifetimes are naturally expected as the expander is operated at lower frequencies of 1Hz-2Hz\textsuperscript{234} and remote cooling of the DC compressor becomes possible. With slow cycles, the design of the regenerator beds are also immensely simplified.

The low drive frequency accommodates the use of much larger regenerator particles (on the order of 0.25 mm diameter) which require less effort to package and contain in comparison to ~0.05 mm particles that would be required for say, a 20 Hz Stirling-cycle coldhead\textsuperscript{235}. This feature is crucial in low temperature applications where the low specific heat of regenerator materials is a severe constraint. The operation of a standard GM refrigeration is illustrated in Figure A5.2.
Figure A5.2: Regenerative Gifford McMachon refrigeration cycle

In the first image, high pressure gas at higher temperatures arrives from the compressor into the expander. This moves the expander to the left, so that the hot gas moves through the regenerator, becoming cooler and experiencing a pressure decrease as a result of the increasing volume at the cold end. The lower pressure at the cold load end (third image) forces the displacer back to the right, and the cold gas heats through the regenerator again, gaining simultaneous increase in pressure before exiting out of the expander into the compressor, where it is compressed, and the cycle begins again.
The operation of the ARS4HW expander is shown in Figure A5.3. In the left image, the cycle begins by opening of the high-pressure valve, where the gas flows through the regenerator to reach the cold end. When the low-pressure valve opens, the cold gas retraces its path out through the low pressure inlet. Additionally, the displacer is pneumatically driven in this system so that mechanical wear and tear and vibrations caused by mechanical movements (prevalent in GM systems) can be minimised\textsuperscript{236}.

As shown above in Figure A5.1, closed cycle He operation comprises an ultrahigh vacuum system since low pressures at the molecular flow of gas are necessary for the cooling operation. The ARS cryostat is thus integrated to a Leybold Oerlikon turbomolecular vacuum pump capable of achieving pressures up to $10^{-9}$ mbar.

In a turbo pump, the rotating rotor blades transfer downward momentum to the air molecules incident on it. As gas molecules drift in a deliberately biased direction upon contact with a solid surface\textsuperscript{237}, the angular position of the stator blades promote their subsequent sequential deflection until they are vented out. Although the operation of turbopump is simple, the process is highly dependent on the thermal velocity of gas.
molecules and the leakage of air molecules necessitating high spin frequencies of the rotor. The Leybold Turbovac 50 spins at 1200Hz or 70000 rpm in the Holweck stage design (screw-type axial compressor).

In axial flow turbo pumps, the rotors and stators are designed to achieve high volumetric speed with minimal compression at the inlet and maximum compression at the expense of volumetric speed at the exhaust line to facilitate efficient outgassing rates. This is evident from the unequal size and aspect ratio of the rotor blades at the inlet and venting flange (exhaust) in Figure A5.4. The turbomolecular pump is generally limited by the inefficiency of pumping low molecular weight gases.

![Figure A5.4: Turbovac 50 (picture adapted from product manual)](image)

Nevertheless, the blades must be located as close to the pump casing wall as possible to prevent leakage and the momentum imparted by the blades on the molecules must be significant compared to the rate of collision between the molecules themselves. For these reasons, turbomolecular pumps cannot be operated in the viscous flow $>10^{-3}$
mbar and require a backing pump to initiate low pressures of <10^{-3}\text{mbar}. The Turbovac 50 is thus assimilated with a Trivac E oil sealed two-stage rotary vane backing pump.

In the Leybold Trivac E pump, an eccentric ring aids the flow of air through the cycle with the use of spring-connected vanes and centrifugal force. A low-pressure environment is initially formed in the system when the vane begins rotating at the inlet, creating a low volume and low-pressure area. As higher pressure air rushes in to fill this pressure difference, it is trapped and compressed by the rotating vane. The reduction in volume as a result of further vane rotation causes an increase in pressure and the air escapes through the exhaust valve.

A gas ballast is used in the Trivac E to prevent condensation of vapours in the pump chamber with supplementary air provided just before the air leaves the exhaust so that overpressure is achieved early. Without a gas ballast, the vacuum pump oil becomes contaminated, as the continual deposition of condensates gradually affects pump performance. This is nonetheless a trade-off, as opening the gas ballast valve in itself increases the pressure levels that can be attained.

Lower pressures can also be obtained with a two-stage pump as it overcomes the pressure limitations in single stage systems due to unavoidable contact of atmospheric air with sealing oil. The two-stage rotary vane pump is illustrated in Figure A5.5.

Figure A5.5: Two-stage rotary-vane pump. Section 1 is the high vacuum stage and 2 the 2nd forevacuum stage. The blue arrows indicate the rotation of the vane through the eccentric ring creating alternating low and high pressure volumes to drive the flow of air (picture adapted from product manual)
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