Room Temperature III-Nitride Quantum Light Sources

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Abstract

A system that is able to produce single photons is a fundamental building block for many quantum technologies. Significant progress has been made in the solid state, where semiconductor quantum dots and defect states in wide band gap materials have been heavily investigated as sources of non-classical states of light. However, only few solid state systems are able to produce single photons at room temperature, removing the requirements for costly cryogenic cooling that limits the practicality of some of today’s highest performance single photon sources. The large bandgaps of binary III-nitride compound semiconductors present an exciting platform for quantum photonics at room temperature. In this thesis, quantum emitters in gallium and aluminium nitride are investigated as a future source of single photons at room temperature. Techniques to enhance the light collection from the source are presented, including a lithography technique to pattern top-down etched structures spatially aligned to emitters in these compound semiconductors of widespread use in present lighting and power electronics technology.
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Chapter 1

Introduction

High-performance modern optical technologies have changed the face of the world. Fast repetition rate lasers enable the modern internet, where an unfathomable amount of data is transmitted around the world through optical fibres. White light LEDs lead to a drastic reduction in the power required to light the world around us. Integrated circuits, that are essential for modern electrical devices from mobile phones to satellites, are patterned and processed using light. It is not unreasonable to suggest that most manufactured items today are in some way made using light. In the future, one of the most fundamental ways in which light is poised to change our world is the exploitation of the quantum nature of light, the photon. In this thesis, III-nitride semiconductors are explored in the context of quantum photonics, focusing on novel quantum emitters in AlN and GaN as promising sources of single photon states.

1.1 Solid State Single Photon Sources

The so-called single photon source is a fundamental building block for many quantum photonic technologies. It is well understood that the photon, a quantum of electromagnetic radiation which follows the wave-particle duality principle, provides a unique physical platform onto which information can be encoded in any of its degrees of freedom: polarisation, time-bin, wavelength or path encoding. In addition, single photons are regarded as largely free of noise, avoiding decoherence from interactions with the environment that plague other physical implementations of quantum systems such as trapped ions [1] or superconducting qubits [2]. The photon can therefore act as a flying qubit, where quantum information can be transmitted across vast distances at the speed of light without loss of information. It has been shown that a linear-optical quantum photonic circuit, along with efficient single photon generation and detection, is sufficient to build a scalable multi-qubit quantum computer [3]. Therefore, significant research attention has been invested in identifying an ideal source of single photons. Whilst a number of physical systems that emit single photons have been developed, and are discussed...
in detail in this chapter, none currently fulfil all the requirements for an ideal single photon source.

1.1.1 The Ideal Single Photon Source

The search for the ‘ideal’ quantum light source is ongoing. An ideal single photon source can be illustrated by considering a system where, if an operator were to hit a switch, one and only one photon would be instantaneously produced. If one considers a two level system which can be electrically or optically excited to produce a photon, such a source would have the following properties:

- **Fast radiative lifetimes**: Nano or pico-second timescale excited state lifetimes, resulting in a larger number of photon per second emit into a single spatial mode, as the single photon rate is limited by the inverse of the spontaneous/stimulated emission lifetime.

- **Polarisation**: Emission into a single polarisation state for polarisation based information encoding.

- **Narrow spectral linewidths**: Linewidths given by the Fourier transform limit, as governed by Heisenberg’s uncertainty principle, where the linewidth is limited due to the uncertainty in time of photon emission due to the finite radiative lifetime of an emitter. This enables the production of indistinguishable (identical) photons.

- **Entangled photons**: Generation of entangled photons, where the photons cannot be described independently and a measurement of the physical properties of one photon instantaneously sets the properties of the second, known as quantum teleportation.

- **Room temperature operation**: Avoid the need for energy consuming and bulky cryogenic cooling systems.

- **Negligible uncontrolled interactions with the environment**: No dephasing or spectral wandering due to interactions with the host environment.

- **Stable emission**: Single two-level system cycling between the electronic excited and ground states of the system with no deshelving to any metastable states, which reduces the sources’ emission efficiency.

- **Single photon purity**: One and only one photon should be produced on demand, where the probability of emitting a photon is 100% with no chance of multi-photon emission events.

- **On-demand generation**: The system emits one and only one photon at an arbitrary time defined by the operator.

- **Electrical pumping**: Electrical excitation of the two-level system to present a triggered source of photons. The electrical device, typically a semiconductor based diode, should be fast and operate ideally with GHz triggering rates.
• Emission wavelength: Photons produced from the source should match the operation wavelength of low-loss optical elements and efficient detectors.

• Integration into optical devices: The source should be easily integrated into other optical systems such as waveguides and cavities for emission enhancement.

The first report of a single photon source was by Kimble et al. [4] using resonant excitation of sodium atoms. Since this report, a large number of devices and material systems have been investigated as a source of non-classical states of light. A number of the most promising sources, including: spontaneous parametric down-conversion, semiconductor quantum dots, two-dimensional materials and defects in wide bandgap semiconductors, are subsequently discussed in detail. An illustration of four families of solid state single photon sources is shown in Fig.1.1.2.

1.1.2 Spontaneous Parametric Down-Conversion

The process of spontaneous parametric down-conversion (SPDC) is a non-linear optical process that converts one high-energy photon into a pair of entangled photons of lower energy. The process follows the laws of conservation of energy and momentum such that the sum of the energies of the resultant photons, often referred to as the signal and idler photons, equals the energy of the pump photon. The process of SPDC was first demonstrated by Harris et al. [5]. Due to the weak nature of non-linear quantum optical effects, the technique suffers from low conversion efficiencies. Extensive efforts have been made into improving this conversion efficiency, using techniques such as confining the pump into waveguides [6]–[8], photonic crystals [9], micro-ring resonators [10], [11] and plasmonic meta-surfaces [12]. To illustrate the conversion efficiency of SPDC-based single photon generation, Block et al. report a photon pair generation rate of $4 \text{ photon pairs per } 10^6 \text{ pump photons}$ [8]. In addition to the low conversion efficiency, the output photon pair statistics follows the Poissonian nature of the laser. To generate single photon states, one can weakly pump the crystal so that the mean photon number is less than one. However, the statistics are still Poissonian, resulting in a finite probability of multi-photon and no-photon emission events.

1.1.3 Quantum Dots

One of the most promising sources of single photons are semiconductor quantum dots (QDs). Thanks to their nanoscale size, where the dot is comprised of a semiconducting material with an electronic band gap different to the host matrix, the QD can confine carriers in all three dimensions. Due to the particle-in-a-box-like confinement, the QD presents a system of discretised energy levels where, once small enough, only a few carriers can be trapped in the dots’ excited/ground state. The QD’s emission and energy structure is both size and shape dependent and confinement as discretised energy levels occur when the dot is smaller than twice the exciton Bohr radius, where the electron and hole in
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Figure 1.1: Overview over major solid state sources of single photons. i-iii) Three regimes for spontaneous parametric down-conversion: type-I (i), colinear type-II (ii) and non-colinear type-II (iii) [13]. iv) Design of an on-chip spontaneous parametric down-conversion source coupled to a separate detector chip [10]. v) Quantum dot light sources coupled to a pillar cavity mode for cavity-enhanced single photon and entangled photon generation [14]. vi) A tunable, free space cavity for single photon generation from quantum dots, demonstrating the greatest to date source-to-detector efficiency of 80% [15]. vii) Illustration of two-dimensional materials based heterostructures for advanced electronic and optoelectronic devices [16]. viii) Confocal scan map of an exfoliated WSe$_2$ flake demonstrating localised single photon emission [17]. ix) Large scale quantum emitter arrays in WSe$_2$ via transfer of a flake onto an array of nano-pillars [18]. x) Energy level structure of the NV$^-$ colour centre in diamond with the optically addressable spin-triplet ground state [19]. xi) Unit cell of diamond showing the configuration of the foreign nitrogen atom and adjacent vacancy that comprises the NV$^-$ colour centre. Confocal scan map showing the localised emission from the NV$^-$ centre [19]. xii) Atomic configuration of the silicon vacancy centre in 4H-SiC [20]. xiii) Spectra and atomic configuration of the carbon antisite–vacancy pair in 4H-SiC [21].
the exciton can be considered as a hydrogen nucleus with reduced mass. Due to the discretised energy levels, QDs are often referred to as artificial atoms. The first QD light source that demonstrated single photon statistics was presented by Michler et al. [22] at the turn of the century. QDs have been investigated as a source of single photons [23–28] that meet many of the requirements of an ideal single photon source, including entangled photon pairs from the bi-exciton cascade [29–31], high brightness [15], transform limited linewidths [32], integration into photonic devices [15], [28], [33], [34], indistinguishable single photons [35], polarised photon emission [36] and electrical pumping by integration into a semiconductor diode structure [36–41]. In addition to the high quantum efficiency of the dots themselves, devices have successfully been fabricated to increase the photon collection efficiency into free space optics, coupling dots to: dielectric nano-antennas (nanowires) [42–45], micro-pillars [14], [28], [46], micro-lenses [47], dielectric bullseye cavities [34], [48]–[50] and free space cavities [15]. In addition to the enhanced collection efficiency, embedding a QD into a cavity leads to the Purcell effect, modifying the spontaneous emission lifetime of the dot. An ongoing research challenge is the growth of site controlled QDs with well defined shapes and sizes [51], [52], overcoming the limitations of self-assembly and the need for a ‘hero’ device correctly coupled to a photonic device or complex predetermination of the dots’ position [53].

The main limitation of the aforementioned research into QD single photon sources is the low-temperature operation due to the use of self-assembled InGaAs/GaAs materials. QDs are typically grown via the Stranski-Krastanov technique, where islands form due to the strain and chemical potential between the binary and ternary compounds. The islands form after a few nanometres of lateral growth, where the 2D lateral layer is referred to as the wetting layer. It is the thermal escape of carriers from the dot to the wetting layer that suppresses the emission of photons at elevated temperatures. Early research to overcome the low temperature requirements of InGaAs dots investigated CdSe/Zn(S,Se) dots [54] which demonstrated single photon statistics up to 200 K temperatures, albeit with a low quantum efficiency and multi-photon emission probability at temperatures above 40 K.

The wide band gap group III nitride (III-nitride) material platform has also been investigated as a host for QD that operate up to room temperature and beyond [26], [55–68]. Integration into cavities [68], recent demonstration of long de-phasing times [67], electrical pumping [69], [70], high single photon purity [71] and site controlled growth via high-crystal quality nanowires [59], [72] make the material platform a promising candidate for high temperature quantum technologies.

1.1.4 Two-Dimensional Semiconductors

The discovery of single photon emitters in two-dimensional (2D) materials led to an explosion of research interest in the field. 2D materials were first synthesised using mechanical exfoliation by Geim and Novoselov [73], where the exfoliation of graphite led to the discovery of graphene, a stable two-dimensional carbon lattice. Since their discovery, the exceptional electronic properties of graphene
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Figure 1.2: Electrically driven solid state single photon sources. i) An InGaAs/GaAs quantum dot embedded in an electrically contacted distributed Bragg reflector cavity [28]. ii) A two dimensional material based quantum dot [105]. iii) A silicon carbide quantum LED which demonstrates single photon statistics at room temperature [106]. iv) GaN/InGaN quantum dot nanowire LED [70]. v) Diamond NV-centre room temperature quantum LED [107].

have been revealed in a large number of reports [73]–[79] with one of the most exciting developments in condensed matter physics being the discovery of Moiré superlattices which form when one atomic layer is rotated on top of a second atomic layer to the so-called ‘magic angle’, leading to superconductivity [80]–[85]. However, graphene does not emit light, and after its inception it was not long until other researchers discovered a whole host of different 2D materials such as hexagonal boron nitride (h-BN) [86], [87] and transition metal dichalcogenides (TMDCs) such as MoS$_2$ and WS$_2$ [88] with direct bandgaps. A decade after the discovery of graphene, the 2D materials MoS$_2$, WS$_2$, WeSe$_2$ and hBN were discovered to emit single photons [17], [89]–[95]. For the TMDCs, the quantum emission is accredited to localised, weakly bound excitons [90], [92]. For hBN, the emission is ascribed to defects deep within the bandgap [94]. Since this discovery, 2D emitters have met a lot of the requirements for the ideal single photon source, including transform limited linewidths [96], [97], short radiative lifetimes (high brightness) [94], [98], electrical pumping [18], [89] and integration with photonic devices [99]–[102]. In addition, the quantum emission that is attributed to deep defect states in the bandgap of monolayer h-BN demonstrates single photon statistics at room temperature [94], [98], [103], [104].

1.1.5 Wide Band Gap Materials

Another widely investigated family of solid state single photon emitters are crystalline defects in wide band gap materials. All wide bandgap materials such as diamond are transparent in the visible spectrum. The energy separation between the conduction and valence band suppresses absorption of visible
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photons, as a visible photon cannot promote an electron from the valence to the conduction band. Atomic impurities such as vacancies and/or foreign atoms modify the local electronic properties of the host, introducing allowed energy levels within the band gap. These energy levels enable absorption of photons with an energy greater than the energy difference between the ground and excited states of the defect. Under high concentrations, the defects change the bulk absorption properties of the materials and can lead to an observable colour change in the appearance of the crystal. As a result, the defects are often referred to as colour centres. Single isolated colour centres often demonstrate single photon statistics even at elevated temperatures, which is attributed to the energy difference between the defect and bulk electronic states, suppressing thermal escape of the carriers.

Of the wide bandgap materials, diamond is the most investigated and hosts a large number of known colour centres. The most widely investigated is the negatively charged nitrogen vacancy centre (NV⁻, hereon referred to as the NV centre). The NV centre was first observed in the mid-to-late 20th century [108]. However, it was not until advances in confocal microscopy that the NV was first individually imaged and measured by Gruber et al. [109]. The authors demonstrated optically detectable magnetic resonance (ODMR) of the spin-triplet ground state of the centre. A number of years later it was shown that the light from the NV centre follows single photon statistics, with an additional power-dependent bunching of the photon statistics [110]–[112]. These early reports on NV centres demonstrated a number of important properties of the colour centres, including the broad emission spectrum [109] and low brightness [110]. It was not long until other colour centres in diamond were investigated as suitable candidates for single photon emitters, including the silicon vacancy centre [113], [114].

Diamond colour centres have demonstrated impressive properties that have enabled their use as: solid state spin qubits with long coherence times [19], [115]–[117], nanoscale sensors of magnetic and electric fields [118], [119], sources of entangled photons [120], quantum memories [121]–[123], room temperature quantum diodes [107], [124] and qubit teleportation [125] to name a few. These demonstrations have made diamond one of the most investigated platforms for quantum technologies. Diamond is inherently difficult to process into a device due to its hardness and missing suitable etchant, as well as its tendency to convert into graphite as a stable material. The poor p-type doping makes high performance electronic devices difficult to realise. However room, temperature quantum light emitting diodes (LEDs) have been demonstrated as illustrated in Fig.1.1.4(v).

In addition to diamond, a number of defect centres have been investigated in compound semiconductors, especially silicon carbide (SiC). SiC has the particular advantage of compatibility with silicon and many of its polytypes have large bandgaps, making them ideal candidates as hosts for room temperature quantum light emitters. In addition, whilst the material is a binary compound, the nuclei can be spin-free [126], eliminating the spin bath that can de-phase solid state spin qubits. To this end silicon carbide has been heavily investigated as a spin-based solid state qubit and has demonstrated coherent control of the confined electron spin [20], [127]–[130] on ms timescales. In terms of the generation
of single photons, the many polytypes of SiC with the numerous colour centres have demonstrated emission across the visible spectrum and into the near infra-red [20], [21], [129], [131]. The emitters in SiC fulfil a lot of the requirements for single photon sources, including: one of the brightest sources to date (without a cavity) [131] and near-transform limited linewidths [132], [133] at low temperatures. SiC hosts single photon emitters at telecoms wavelengths [128], a desirable emission band for fibre and free-space based quantum communications. In addition, the processing of SiC-on-insulator presents an exciting platform for integrating solid state spins into an on-chip photonic network [134].

1.2 III-Nitride Semiconductors

Of all the compound semiconductors, the III-nitride family are arguably the most commercially important material system to be investigated over the last half century. This is largely due to the direct electronic band gaps of the binary compounds, where the energy minimum of the valence and conduction band overlap in momentum space, and the hardness of the compounds, enabling high performance optoelectronic and electronic devices. Indeed, the 2014 Nobel prize in physics was awarded to Akesaki, Amano and Nakamura for their pioneering work into gallium nitride (GaN) based blue light emitting diodes [135], enabled by the discovery of suitable p-type doping with magnesium (Mg) [136]. This was a technological breakthrough that redefined white-light lighting for the 21st century. Since then, GaN and its accompanying binary III-nitride compounds indium nitride (InN) and aluminium nitride (AlN) have been successfully used to create high performance UV light emitters [137]–[139], LEDs [140]–[142], lasers [143]–[146], high-power transistors [147], CMOS logic gates [148] and even for splitting water to produce sustainable fuels [148]. An illustration of a III-nitride UV LED (i), a CMOS integrated circuit (ii), integrated photonics platform (iii) and an integrated quantum photonics platform (iv) are shown in Fig.1.2.1.

1.2.1 Physical Properties of III-Nitrides

The aforementioned technological demonstrations using III-nitride binary and/or ternary compounds are enabled due to the unique properties of the material family. For all of the binary compounds, the most thermodynamically stable crystal form is the hexagonal Wurtzite structure. Each group-III atom is tetrahedrally bonded next to four nitrogen atoms, arranged in a ABABAB stacking sequence. The lack of inversion symmetry due to the non-centrosymmetric structure along the [0001] axis, the common growth axis for the crystal [149], and the finite dipole moment associated with the group III and metallic element leads to a built-in electric field, piezoelectricity and pyroelectricity. It is the internal electric field, along with strain and defect formation at high indium concentrations, that limits the creation of light emitting devices across the whole visible spectrum from ternary InGaN, leading to the so called ‘green gap’. Any InGaN/GaN quantum well based heterostructure results in
a finite piezoelectric polarisation difference between the InGaN and GaN epilayers. This results in an electric field across the interface, directly opposing the internal electric field. This leads to a bending of the electronic bands and a separation of the electron and hole wavefunctions, referred to as the quantum confined stark effect (QCSE), reducing the oscillator strength and efficiency of the device. As the indium incorporation in the ternary compound and/or the size of the quantum well is increased the wavefunction overlap decreases. In addition to the reduced oscillator strength. A red-shifting of the photoluminescence wavelength is also observed due to a change of energy of the electron and hole levels in the quantum well. When the quantum well is too thick or the indium concentration is too high, then the small overlap and electric field leads to carriers preferentially tunnelling out of the heterostructure, suppressing optical emission. To overcome these issues, significant research has been invested into semi-polar and non-polar devices that utilise, for example, the semi-polar \( \{20\overline{2}1\} \) plane \[150\], \[151\].

### 1.2.2 Epitaxy of III-Nitrides

One of the biggest research challenges for III-nitrides is the epitaxial growth of single mono-crystalline material layers. GaN and AlN can be grown using either metal-organic chemical vapour deposition (MOCVD) or molecular beam epitaxy (MBE) \[149\], as the high melting temperature of the compounds (\( > 2200^\circ\text{C} \)) and high required nitrogen pressure limits crystallisation from melts. The fundamental...
requirements for large-scale single crystalline relaxed growth of any material is to use a substrate material that is matched in terms of its thermal expansion coefficient and lattice constants. Unfortunately, no substrate that matches the lattice constant of GaN or AlN is known, and typical substrates used in their epitaxy are sapphire, SiC or [111] silicon. As an example, the most widely used substrate material for GaN epitaxy is sapphire, which has a lattice mismatch with GaN of 16% \(154\). The lattice mismatch induces stresses in the crystal as it grows, which can only be reduced by forming various dislocations and stacking faults. After a while the stress in the crystal is reduced, and the crystal growth is relatively stress free. Unfortunately for the nitrides, threading dislocations are common which can extend all the way to the surface of the crystal. For gallium nitride, one technique that is commonly used to mitigate the lattice mismatch between the sapphire and semiconductor is to exploit the growth of a thin AlN \(155\) or GaN \(156\) buffer layer, which traps dislocations at the substrate-epilayer interface.

### 1.2.3 Integrated Photonics and Quantum Photonics

In the context of integrated photonics, the III-nitrides present a promising platform for high-performance integrated devices and systems. For any integrated photonic platform a number of physical properties are desirable. Intuitively, the minimal requirement for integrated photonics is that the material of interest is transparent across the desired spectral window. The III-nitrides, due to their wide bandgap, which for wurtzite GaN and AlN are 3.4 and 6.2 eV \(157\) respectively, results in transparency across the visible spectrum and into the infra-red. Beyond optical transparency, desirable functions of the crystal include linear electro-optic (Pockels effect) for high-speed modulation, \(\chi^{(2)}\) non-linearity (which forms the basis for the Pockels effect) for wavelength conversion and low thermo-optic coefficients \(\delta n/\delta T\). AlN is arguably the most promising III-nitride platform for integrated photonics due to its transparency, high crystal quality and values for the aforementioned parameters, including: \(\delta n/\delta T = 2.32 \times 10^{-5} \text{ K}^{-1}\) \(158\), \(\chi^{(2)} = 4.7 \text{ pm V}^{-1}\) \(159\) and a propagation loss of 0.6 dB cm\(^{-1}\) \(160\) at 1550 nm. Due to these properties, a number of key integrated photonic devices have been successfully demonstrated in AlN including: low-loss optical waveguides \(160\), micro-ring resonators \(159\), \(161\), second harmonic generation \(159\), GHz frequency electro-optic modulation \(160\), frequency-comb generation \(162\), grating couplers \(163\), nano-mechanical coupling of photons and microwaves \(152\), photonic cavity nano-beams \(164\), \(165\) and integration on silicon \(166\). A very recent demonstration by Noel et al. \(153\) illustrates AlN’s capabilities as a platform for quantum optics, where they nano-position diamond-based quantum emitters onto a patterned AlN-on-sapphire photonic circuit. This pioneering work suggests that aluminium nitride is the material of choice for wide bandgap integrated photonics.
1.3 Thesis Outline

In this thesis, the III-nitrides, specifically GaN and AlN, are explored as a platform for practical quantum information processing. To this end, the rest of the thesis is organised in the following chapters:

- Chapter 2 - The experimental methodology that enables the optical and photon-counting measurements in this thesis are introduced.

- Chapter 3 - A new family of room temperature quantum emitters in AlN is introduced and discussed in detail. Spectral, power-dependent, temperature-dependent and time-resolved photon-counting measurements are used to investigate the properties and quantum nature of the emitters.

- Chapter 4 - The finite difference time domain simulation approach is introduced to enable quantifying the enhancement in light collection using photonic nano/micro-structures. To this end, the solid immersion lens and two top-down etched structures are investigated analytically and numerically.

- Chapter 5 - The hemispherical solid immersion lens is investigated in detail. Experimental data for the collection efficiency enhancement for a millimetre size lens are compared to numerically and analytically predicted values. The enhanced imaging of quantum emitters in high refractive index materials is investigated with a quantum emitter in gallium nitride. The coupling of light through a thin spacer between the lens and the semiconductor is investigated using a statistical analysis over 500 emitters in aluminium nitride.

- Chapter 6 - An in-situ photo-lithography technique is developed to deterministically pattern photonic structures on/around quantum emitters in compound semiconductors.
Chapter 2

Experimental Methods

In this chapter, the experimental methods to enable single photon spectroscopy are introduced. We
begin by discussing the custom designed confocal microscopes that enable single emitter spectroscopy
at ambient and cryogenic temperatures.

2.1 Laser Scanning Confocal Microscopy

Confocal microscopy has become a technique used in a number of scientific disciplines thanks to
the enhanced resolution and contrast relative to that of a conventional wide-field microscope. The
principle is simple - a spatial filter in the form of a confocal pinhole is used to remove out of focus
light forming in the image. In traditional wide-field microscopy, the sample is flooded with light and
the reflection/fluorescence is collected onto a detector, including a large portion of the image that is
out of focus. In contrast, a laser scanning confocal microscope (LSCM) exploits point illumination
(and detection), where typically a monochromatic light source such as a laser is focused to a single
point.

The optical volume excited via point illumination in an aberration free optical system is determined
by the numerical aperture (NA) of the focusing lens, the wavelength of the excitation source (\( \lambda \)) and
the refractive index (\( n \)) of the medium being imaged. The optical volume follows a three-dimensional
diffraction pattern associated with focusing a non-ideal light source, a Gaussian laser beam, to a single
point. With confocal microscopy it is possible to improve on the resolution by spatially filtering the
high-order diffraction modes of the focused point, leaving only the first order of the diffraction pattern.
This is achieved by engineering the collection confocal pinhole diameters \( d_{PH} \) to that of 1 Airy disk,
which defines the Airy unit (AU),

\[
    d_{PH} = 1.22 \frac{\lambda}{NA} = 1 \text{ AU}. \tag{2.1}
\]

In addition to improved lateral resolution, spatially filtering the three dimensional diffraction pattern
Chapter 2. Experimental Methods

results in a reduction of the diffraction volume in the axial direction, leading to a reduced focal ‘depth’ in the sample, enabling optical sectioning of a sample. Due to the complexity of deriving the exact point spread function (PSF) of a confocal microscope, the resolution of the optical system is often approximated using the full width half maximum (FWHM) of the Airy disk. It is experimentally convenient to define the spot size as the Airy disk FWHM, which results in a lateral and axial resolution of 167.

\[
R_{\text{lateral}} = 0.51 \frac{\lambda_{\text{exc}}}{\text{NA}},
\]

(2.2)

\[
R_{\text{axial}} = 0.88 \frac{\lambda_{\text{exc}}}{n - \sqrt{n^2 - \text{NA}^2}},
\]

(2.3)

where \(n\) is the refractive index of the immersion medium for the lens. It is apparent that the axial and lateral resolution is governed by the excitation wavelength \(\lambda_{\text{exc}}\). This expression holds true assuming that \(d_{\text{PH}}\) is greater than the size of the Airy disk, and as such the PSF of the detection arm \(\text{PSF}_{\text{col}} > \text{PSF}_{\text{exc}}\). At the limiting case of \(\text{PSF}_{\text{col}} \approx \text{PSF}_{\text{exc}}\), where \(d_{\text{PH}} < 0.25 \text{ AU}\), wave-optical image formation laws dominate and the resolution is governed by the effective PSF of the microscope \(\text{PSF}_{\text{eff}}\). Mathematically, \(\text{PSF}_{\text{eff}}\) is governed by the convolution between the excitation and collection intensity PSFs in the following form,

\[
\text{PSF}_{\text{eff}} = \text{PSF}_{\text{exc}} \otimes \text{PSF}_{\text{col}}.
\]

(2.4)

The fluorescence \(\lambda_{\text{col}}\) and excitation \(\lambda_{\text{exc}}\) wavelengths are considered by taking the mean \(\lambda_m\) in the following form,

\[
\lambda_m = \sqrt{\frac{\lambda_{\text{exc}} \lambda_{\text{col}}}{\sqrt{\lambda_{\text{exc}}^2 + \lambda_{\text{col}}^2}}},
\]

(2.5)

The axial and lateral resolution in Eq.2.2 and Eq.2.3 are transformed to 167,

\[
R_{\text{lateral}} = 0.37 \frac{\lambda_m}{\text{NA}},
\]

(2.6)

\[
R_{\text{axial}} = 0.64 \frac{\lambda_m}{n - \sqrt{n^2 - \text{NA}^2}}.
\]

(2.7)

2.1.1 The Room Temperature Microscope

The room temperature optical measurements in this thesis were taken using a custom laser scanning confocal microscope (LSCM). To illustrate the design of the LSCM, shown in Fig.2.1, we follow the excitation source through the microscope. A frequency-doubled Nd:YAG laser (532 nm) is coupled into
single mode fiber (SMF) using mirrors M7 and M8 to provide point illumination for the microscope. Coupling the laser into SMF is optimised by matching $1/e^2$ intensity Gaussian beam waist to the mode field diameter (MFD), where the MFD is the physical measure of the irradiance at the end of the SMF. The focal length $f$ of L7 in Fig. 2.1 is designed to optimise the coupling using the following relation,

$$MFD = \frac{4\lambda f}{\pi w},$$

where $f$ is the focal length of L1 and $w$ is the $1/e^2$ intensity Gaussian beam size of the laser. The excitation source is subsequently coupled out of the SMF and into the microscope using L1, with a beam size of $w = 3.4\text{ mm}$. The focal length of L1 is designed to match the back pupil size, $w_b = 2 \times NA \times f$, of the objective lens M0 with a filling factor $F_f = w/w_b \approx 1.1$ to compromise resolution and excitation power. The objective lens M0 is the EC Epiplan-Neofluar 100x/0.9 from Zeiss with a 1 mm working distance and a high $NA = 0.9$. The collected fluorescence from a point source is collimated by M0 and propagates through the microscope with a Gaussian profile. The fluorescence is separated from the excitation beam using a dichroic beamsplitter BS1 with additional filtering F2 to suppress the reflection of the laser when imaging objects close to the sample surface. The fluorescence is coupled into SMF by the lens L4, where the MFD acts as the collection pinhole. The focal length was designed to be close to the ideal focal length given by Eq. (2.8) considering the beam waist radius.
Chapter 2. Experimental Methods

Figure 2.2: Illustration of the working principle of the 4f optical system.

as governed by the product of the NA and effective focal length of the objective lens M0. Spatial
overlap of the excitation and collection position is achieved using the mirrors M1, M4 and M5.
In order to form an image of the sample the excitation and collection are scanned across the sample.
This can be achieved by moving the sample in a controlled manner, either by a motorised or a
piezoelectric sample stage. Mechanical movement, however, is a slow process, prone to mechanical
and/or electrical drift. Another technique to achieve scanning on the sample is to scan the beam in
the plane of the sample using a scanning laser system. This exploits the optical effect of a 4f focal
system, also referred to as an optical relay. This system translates a collimated beams change of angle
of incidence $\Delta \theta$ onto the first optical element into a XY displacement on the sample. This is achieved
by using two lenses, L2 and L3 in Fig 2.1 as well as a single or dual-axis mirror M2. The dual-axis
galvanometer mirrors in Fig 2.1 are placed a focal length away from the first lens L2, and two focal
lengths away from L3, focusing the beam between the two lenses. The objective lens M0 is placed
another focal length away from L3, totalling a four focal length optical system, hence 4f. This acts
to translate this change in angle into a change of displacement $\Delta D$ on the sample. For the simplest
configuration of identical focal length lenses L2 and L3, the change in displacement on the sample
plane is governed by the trigonometric relation,

$$\Delta D = f_e \times \tan(\Delta \theta),$$

where $f_e$ is the effective focal length of the objective lens and $\theta$ is the optical angle of the mirrors.
An illustration of the working principle of the 4f optical system used in the microscope and how it
translates to a displacement on the sample surface is presented in Fig 2.2.

Wide-field imaging of the sample is achieved in conjunction with confocal imaging using the white
light imaging path in Fig 2.1. A beamsplitter BS3 combines the illumination from a white-light LED,
collimated using a NA = 0.6 aspheric condenser lens L5, with the reflection image from the microscope.
A removable beamsplitter BS2 combines the confocal and wide-field imaging. The beamsplitter BS2
is removed to avoid losses for fluorescence measurements.
2.1.2 Polarisation-Resolved Spectroscopy

Polarisation-resolved microscopy was achieved for the microscope in Fig. 2.1 by incorporating polarisation optics in the excitation and/or collection beam paths. To enable polarisation dependent excitation measurements, the > 50 : 1 polarised Nd:YAG laser is coupled into polarisation maintaining (PM) SMF aligned to the slow axis of the fiber. This preserves the polarisation of the laser through the fiber. Alignment of the polarisation to the axis is achieved using the linear polariser LP3 and a half wave plate (HWP). A Faraday rotator FR1 is used to isolate the Nd:YAG laser from back reflections. On the excitation path of the microscope, a HWP is placed as close to the sample as possible. Placement of the HWP on the excitation path decouples the excitation and collection polarisation. An additional polariser LP1 is used to clean up the excitation polarisation out of the PM fiber. For emission polarisation resolved measurements, a thin film linear polariser LP2 is rotated in the XY plane of the microscope.

Careful consideration was made to mitigate the change of linear polarisation through the microscope. Three losses were considered. The finite displacement of the beam when rotating a thick optic in the beam path was mitigated by ensuring that the excitation and collection optics were placed as close to the sample and detector, respectively. If one considers the excitation path through the microscope from the SMF to the objective lens, the HWP is placed before the beamsplitter BS1. In principle, one could place the HWP just before the objective lens. This would avoid displacing the excitation PSF away from the collection PSF as one rotates the optics. However, this rotates both the excitation and collection polarisation. To accurately determine the collection polarisation, one would have to consider the rotation at both the HWP before the objective and the linear polariser LP2. For simplicity, the rotation stage was placed on the excitation arm of the the beamsplitter and it was ensured that the beam was as close to normal incidence as possible with the optic.

Rotation of a polarised beam across the face of an non-normal optic changes the reflectivity/transmissivity. This is often referred to as diattenuation and is unavoidable at finite angles of incidence. In addition to diattenuation, rotating an optic across a birefringent material such as a dielectric beamsplitter leads to a phase change between the ordinary and extraordinary axis. This results in a retardance of the polarisation state, which is projected onto any measurement. Both the retardance and diattenuation can be mitigated by reducing the angle of incidence on optical components such as beamsplitters and dielectric mirrors. The retardance can be avoided by using complementary optics where the ordinary axis is aligned to the extraordinary axis of the second optic. This acts to cancel out the retardance introduced by the first optic.
2.1.3 The Low Temperature Microscope

For cryogenic and temperature dependent measurements, a second custom microscope was used. Designed around the same principles introduced for the room temperature microscope, the low temperature microscope is a custom optical head for the AttoDry1000 closed-cycle cryostat which is illustrated in Fig.2.3. The AttoDry is a top loading cryostat, with a tubular sample space. The sample space is optically accessible through an optical window OW. The beamsplitter BS1 combines the excitation and collection. BS2 combines the optical imaging. BS3 is used to combine the LED illumination with the microscope image, which is focused onto the camera using a long focal length aspheric lens L3. The LED is collimated using an aspheric condenser lens L4. Spectral filtering is achieved using F1 and F2. The excitation and collection is coupled into and out of the microscope by focusing into SMFs. The MFD acts as the confocal pinholes for point illumination and detection, respectively.

2.2 Time-Correlated Photon Counting

The coherence properties of electromagnetic fields, i.e. their ability to interfere, can be characterised and explored using a set of \( n^{th} \)-order correlation functions. In order to explain coherence mathematically, the correlation between electric field components was used to define coherence, which can be measured to an arbitrary number of functions. The coherence and interference observed in famous optical experiments, for example Young’s double slit experiment and the Mach-Zehnder interferometer, is of the first order coherence. Robert Hanbury Brown and Richard Twiss (HBT) in 1956 were the first to measure the second order correlation of light. Using two spatially distinct detectors they measured the angular size of the star Sirius [168], [169]. The interferometer in the experiment is used extensively...
in quantum optics to determine the photon statistics of light sources.

2.2.1 The Second Order Correlation Function

The second order correlation measurement can be understood by considering photons arriving on a beamsplitter. The experimental setup, often referred to as the HBT interferometer, is shown in Fig. 2.4 (iv). The stream of photons are split onto two single photon sensitive detectors. In the start-stop configuration, one detector is used as a ‘start’ channel and the second detector registers a ‘stop’.

On detection of a photon, the start detector sends an electrical signal to a time-correlated single photon counting (TCSPC) device which waits for a photon arrival event on the stop channel. The TCSPC builds a histogram of coincidence counts between start and stop times, where the shape of the histogram is determined by the statistics of the photon stream. A time delay on the second channel can be included to create an artificial time zero. This enables the measurement of coincidences before zero delay at the beam splitter.

Measuring photon coincidences in this “start-stop” configuration can lead to the so called ‘pile up’ effect. For bright sources, the probability of detecting long timescale coincidences decreases. This
materialises as an exponential decay in the histogram coincidences where the timescale of the delay
is the inverse of the rate of detection of photons.
A method to overcome the pile up is to record the arrival time of each photon detection event and
post-process the coincidences, hereon referred to as “time-tagging”. The time-tagged post-processing
is done in the following manner. Each photon arrival event on detector one is correlated to every
photon on detector two that arrives \( t \pm t_{\text{search}} \), where \( 2 \times t_{\text{search}} \) is the time span for the histogram and \( t \) is the photon arrival time on channel one. This correlates each detection event on channel one with
every photon that is detected on channel two within the search window. Correlating all photon arrival
events within the time window eliminates the preferential detection of photons at shorter timescales.
The downside is the computational cost associated with correlating every photon arrival event within
\( \pm t_{\text{search}} \).

2.2.2 Photon Statistics

To understand the shape of the histogram measured in the HBT experiment we consider the statistics
of the photon stream. The second order correlation function \( g^{(2)}(\tau) \) written with quantised electric
field operators in terms of the photon creation \( \hat{a}^\dagger \) and annihilation operators \( \hat{a} \) is given in the form
\[ g^{(2)}(\tau) = \frac{\langle \hat{a}^\dagger(t)\hat{a}^\dagger(t+\tau)\hat{a}(t)\hat{a}(t+\tau) \rangle}{\langle \hat{a}^\dagger(t)\hat{a}(t) \rangle^2}, \] (2.10)
where the notation \( \langle ... \rangle \) represents the quantum mechanical expectation value, which can be considered
the average over all possible outcomes of a measurement. At \( \tau = 0 \) \[ g^{(2)}(0) = \frac{\langle \hat{a}^\dagger\hat{a}^\dagger\hat{a}\hat{a} \rangle}{\langle \hat{a}^\dagger\hat{a} \rangle^2}, \] (2.11)
which can de understood as the probability of detecting two simultaneous photons, normalised by
the probability of detecting two photons. The second order correlation function can be considered in
terms of the photon number, where the photon number can be understood as the number of photons
in an arbitrary time bin. The variance of the photon number distribution \( V_n \) is given as as a function
of the photon number \( n \) in the following form,
\[ V_n = \langle n^2 \rangle - \langle n \rangle^2, \] (2.12)
which considering \( n = \hat{a}^\dagger\hat{a} \) and using Eq.2.11 yields,
\[ g^{(2)}(0) = 1 + \frac{(V_n - \langle n \rangle)}{\langle n \rangle^2}. \] (2.13)
The second order correlation function at time zero can therefore be expressed in terms of the variance
and mean of the photon number. The variance of coherent, chaotic and quantised light is known,

\[ \begin{align*}
V_{n, \text{chaotic}} &= \langle n \rangle + \langle n \rangle^2 \implies g^{(2)}(0) = 2, \\
V_{n, \text{coherent}} &= \langle n \rangle \implies g^{(2)}(0) = 1, \\
V_{n, \text{quantised}} &= 0 \implies g^{(2)}(0) = 1 - \frac{1}{n}.
\end{align*} \]

The probability \( P(n, \langle n \rangle) \) of detecting \( n \) photons with a mean photon number \( \langle n \rangle \) is shown for the three light states in Fig.2.4.(i-iii). Coherent light, which describes the photon distribution of a laser, follows a Poissonian distribution around the mean photon number. Chaotic light follows a Bose-Einstein distribution where the greatest probability is always at \( n = 0 \) distribution. This can be understood as photons bunching together in time. Ideal antibunched light follows a Kronecker delta function, with zero probability of \( n \neq \langle n \rangle \), i.e. the variance of the photon number \( V_n = 0 \). For antibunched light, the photon number determines the value of the second order correlation function at time zero. For a pure single photon source, where there is only ever one photon in each time bin, \( n = 1 \) and \( g^{(2)}(0) = 0 \). Any multi-photon time bin with \( n > 1 \) therefore increases the \( g^{(2)}(0) \) value. As \( n \) tends towards infinity the photon statistics tend towards a coherent light source with \( g^{(2)}(0) = 1 - 1/\infty = 1 \). The threshold of \( n = 2 \) is often used to determine the measurements of a single photon source in pulsed excitation measurements, where \( g^{(2)}(0) = 0.5 \).

### 2.2.3 Experimental Considerations

#### 2.2.3.1 Unbalanced Background Correction

Whilst the second-order correlation function for a single photon light source leads to a value of \( g^{(2)}(0) = 0 \), in practice this is never measured. A number of practical considerations must be included in the analysis of experimental data. The most intuitive consideration would be to include any stray light that may reach the detectors during the measurement time. Due to the random nature of any stray light the photon statistics follow a Poissonian distribution. Any Poissonian contribution acts to diverge the value at time zero away from zero towards unity. In addition to stray light, a finite number of dark counts from the detectors, which for avalanche photodiodes occurs due to random thermal excitation of carriers triggering the avalanche process, can act to increase the value at time zero. If one considers the photon arrival time on each detector one can imagine how stray detection events increase the chance of two simultaneous events on both detectors. The \( g^{(2)}(0) \) value is therefore dependent on the signal to noise ratio (SNR). In general, one can account for the stray light using a correction expression.
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\[ g_c^{(2)}(\tau) = \frac{g_n^{(2)}(\tau) - (1 - p^2)}{p^2} \quad \text{where,} \quad p = \frac{C_s}{C_s + C_b}. \quad (2.14) \]

This facilitates correcting the normalised \( g_n^{(2)}(\tau) \) function with respect to the signal count rate \( C_s \) and the background count rate \( C_b \), assuming balanced detection rates on each detector. For the case where the background or signal rates are not balanced the analysis is more involved. Eq.2.14 is expanded in the following form,

\[ g_c^{(2)}(\tau) = g_n^{(2)}(\tau) \left( \frac{C_s^2 + 2C_{sb} + C_b^2}{C_s^2} \right) - \frac{2C_{sb} + C_b^2}{C_s^2}, \quad (2.15) \]

where,

\[ C_s^2 = C_{s1}C_{s2}, \quad C_b^2 = C_{b1}C_{b2} \quad \text{and,} \quad C_{sb} = C_{s1}C_{b2} + C_{s2}C_{b1}, \quad (2.16) \]

leading to,

\[ g_c^{(2)}(\tau) = g_n^{(2)}(\tau) \left( \frac{C_s^2 + \alpha}{C_s^2} \right) - \frac{\alpha}{C_s^2} \quad \text{and,} \quad \alpha = 2(C_{s1}C_{b2} + C_{s2}C_{b1}) + C_{b1}C_{b2}, \quad (2.17) \]

where the subscript differentiates the two detector channels. This lengthy expression allows one to correct the \( g^{(2)}(\tau) \) data for background detection rates that are unbalanced. An illustration of the impact of the signal-to-noise (SNR) ratio is shown in Fig.2.5.(i). High signal to noise ratios, in the order of \( >100:1 \), are required to measure \( g^{(2)}(0) \) close to zero.

### 2.2.3.2 Detector Time Jitter

In addition to the random background noise introducing a systematic offset to the \( g^{(2)}(0) \), the timing electronics can play a role in determining the accuracy of the measurement. In order to accurately determine the \( g^{(2)}(0) \) value, one must consider the time jitter of the detectors and the time-bin of the resultant histogram.

The statistical variation between the photon arrival time and the subsequent electrical output pulse from a detector is known as the time jitter (time resolution). Variations in photon travel depths in the absorber of an APD lead to a variation in the carrier-transit time from the depletion region to the multiplication region [173], [174], which is additionally impacted by the statistical build up of the avalanche process itself [175]. The time jitter of the HBT measurement with two detectors approximates a Gaussian function in the form,

\[ j(t - \tau) = \frac{1}{\sqrt{2\pi\sigma}} e^{-\frac{(t-\tau)^2}{2\sigma^2}}, \quad (2.18) \]

where \( \sigma \) is the FWHM of the Gaussian function and \( \sigma \) is the time jitter value as determined from
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experiments. The measured \( g^{(2)}(\tau) \) can be described including the time jitter mathematically by convolving the normalised \( g^{(2)}_{\text{n}}(\tau) \) function with the measurement response function \( j(t - \tau') \),

\[
g^{(2)}(\tau) = \int_{-\infty}^{\infty} g^{(2)}_{\text{n}}(\tau')j(t - \tau')d\tau',
\]

where the \( g^{(2)}(\tau) \) function can be normalised by the product of the rates on each detector \( \Gamma_1, \Gamma_2 \), the measurement integration time \( T \) and the histogram bin width \( w \),

\[
g^{(2)}_{\text{n}}(\tau) = \frac{g^{(2)}(\tau)}{\Gamma_1\Gamma_2wT}.
\]

An illustration of the effect of finite time jitter of the detectors is illustrated in Fig.2.5.(ii) for detectors with a time jitter equal to the antibunching lifetime (red), half the lifetime (green) and two orders of magnitude smaller (blue). A dependence on the jitter is observed, where the \( g^{(2)}(0) \) increase above zero as the jitter timescale approaches the antibunching timescales.

2.2.3.3 Histogram Bin Width

The bin width of the histogram also plays a role in determining the value of the second order correlation function at time zero. Considering a histogram with bin width \( t_{\text{bin}} \), all photon arrival events in the time bin \( [\tau_i - t_{\text{bin}}/2, \tau_i + t_{\text{bin}}/2] \) are counted to measure \( g^{(2)}(\tau) \). Therefore, for an ideal antibunched source,

\[
g^{(2)}(\tau) = \int_{\tau_i - t_{\text{bin}}/2}^{\tau_i + t_{\text{bin}}/2} (1 - e^{-|\tau|/\tau_0})d\tau.
\]

The effect of finite time resolution is illustrated in Fig.2.5.(iii). When the histogram bin width \( t_{\text{bin}} \ll \tau_0 \) the effect on the finite time resolution is negligible. As the bin width approaches the antibunching lifetime \( \tau_0 \), the bin width introduces a systematic offset to the \( g^{(2)}(0) \) value similar to the finite time jitter.

As the value at time zero for the second order correlation measurement is extensively used to quantify the ‘purity’ of the single photon stream, it is worth understanding the experimental environment and timing resolution of the detectors/electronics used. In this thesis, photon counting is achieved using silicon avalanche photodiodes (APDs) that are sensitive to single photons across the 400 – 1000 nm wavelength window, with a peak quantum efficiency of 70 % at 650 nm and an average timing resolution (jitter) \( \sigma = 350 \text{ ps} \). The output TTL pulse from the Excelitas SPCM-AQRH APDs are counted on an ID Quantique ID900 time controller for time-correlated single photon counting (TCSPC) with a timing resolution, i.e. a minimal histogram bin width, of 100 ps. Considering the timing electronics and detectors used, as well as the effect of finite bin width and detector jitter, one can determine the lowest measurable \( g^{(2)}(0) \) value for a typical antibunching lifetime of \( \tau_0 = 4 \text{ ns} \) is given by,
Figure 2.5: Illustration of systematic errors in second order correlation measurements due to the signal-to-noise ratio (i), detector timing jitter (ii) and histogram bin width (iii) for an ideal antibunched light source with \( g^{(2)}(0) = 0 \).

\[
g^{(2)}(0) = \frac{1}{0.1} \int_{-0.5}^{0.5} \left( \int_{-\infty}^{\infty} (1 - e^{-|\tau'|/\tau_0}) \frac{1}{\sqrt{2\pi 0.35}} e^{-\frac{(t-\tau_0)^2}{20 \cdot 0.35}} d\tau' \right) d\tau = 0.012. \tag{2.22}
\]

Therefore, one can conclude that the experimental setup is suitable for determining the purity of single photon sources with nano-second emission timescales.
Chapter 3

Aluminium Nitride Quantum Emitters

3.1 Introduction

Efficient single photon sources are a key building block for quantum information processing. To date, a small number of material systems are able to produce single photons at room temperature. The recently discovered and least understood family of emitters are colour centres in the III-nitrides, a material family that includes the most widely used compound semiconductor, gallium nitride (GaN). In this chapter, a new family of quantum emitters are introduced, visible emitters in aluminium nitride (AlN). The optical properties of the quantum emitters are investigated using laser scanning confocal microscopy (LSCM). Spectral, power-dependent, temperature dependent and time-resolved photon-counting measurements are used to investigate the optical properties of the emitters, providing an insight into the origin of the emission.

3.1.1 Review of the Literature

Quantum emission from colour centres in GaN was first discovered by Berhane et al. [176]. Using confocal microscopy, they discovered emission spanning from the visible part of the electromagnetic spectrum out to the near-infrared from point-like sources in a GaN-on-sapphire template. Measurements of the photon statistics demonstrated both antibunching and bunching at room temperature. They used density-functional theory (DFT) simulations to attribute the emission to point defects in proximity to nanoscale cubic inclusions in the otherwise wurtzite host crystal. This hypothesis was supported by Zhou et al. [177] where the authors report quantum emission in the telecoms band from a magnesium doped GaN-on-sapphire substrate. Using an etched sapphire substrate and an oil-immersed microscope objective they were able to measure photon rates in the megahertz range due to the patterned substrate directing light towards the optics and the efficient superconductor single-photon detectors (SSPDs). The authors support the hypothesis that the emission originates from a point defect near a cubic inclusions in the host, suggesting that the wide spread of emission
wavelengths cannot materialise due to variations in the localised strain environments but likely from the variations in the internal electric field due to the number of cubic stacks. They attributed the emission to an exciton recombination where the hole is confined in the point defect and the electron is loosely confined in the cubic/wurtzite stacking layers. It is suggested that the exciton binding energy and wavelength of the zero-phonon line (ZPL) are therefore affected by the relative location of the point defect with respect to the cubic inclusion.

A detailed early investigation into the physics of the emitters in GaN was reported by Berhane et al. [178]. Using low temperature spectroscopy on a number of different emitters they demonstrated the broad emission range of the ZPL of the emitters, from 1.736 eV (714 nm) to 1.983 eV (625 nm). A measurement of 19 emitters in the sample gave a mean linewidth of the ZPL at 4K of 3.4 ± 1.1 meV, approximately seven times smaller than the room temperature linewidth, but still three order of magnitude greater than the lifetime-limited linewidth as determined from time-resolved photoluminescence (PL) measurements. They noted that a similar broadening of the natural linewidth from quantum dots in GaN and InGaN [55] had been observed and attributed to ultra-fast spectral diffusion, likely due to oscillating localised charge traps causing spectral wandering of the emission energy due to the Stark effect. Time-resolved spectral measurements were taken where the spectrum from three emitters across the ZPL energy range was measured every second for two minutes. The measurements show a clear shift in the ZPL energy as a function of time for two of the three emitters, emphasised by a fit to each of the spectral measurements. The dynamics of the spectral wandering were not investigated in detail.

In contrast to the previous reports, Nguyen et al. [179] hypothesised that the emission originates from few-site atomic complexes similar to the NV- centre in diamond. They grew a number of different GaN samples using metal-organic chemical vapour deposition (MOCVD) epitaxy. They investigated the impact of extended threading dislocations (TDs), a crystallographic defect that occurs due to the significant lattice mismatch between the substrate and GaN epilayer and can extend through the epilayer to the crystal surface, using a number of different characterisation techniques. Atomic force microscopy was used to measure the surface morphology between eight different samples, six on sapphire and two on silicon. They used confocal microscopy to optically address the defects, where scan maps revealed a variation in the density of emitters, and autocorrelation measurements with tight spectral filtering isolated emitters illustrating the quantum nature of the light emission. Using tunnelling electron microscopy (TEM), panchromatic cathode luminescence (CL) and confocal PL measurements they were able to map the same area of their samples and attempted to correlate the position of the emitters with the extended threading dislocations. They concluded that there was no spatial correlation between the emitters and TDs. However, there was a rough correlation between the number of emitters with the number of TDs. Interestingly, the authors observe no emission from samples grown on silicon. They ultimately conclude that the formation of the emitters was likely due
to a complex impurity and/or point defect in the GaN epilayer, similar to the few-atom sized defects in diamond or silicon carbide [180].

The properties of quantum emitters in aluminium nitride (AlN) have only been briefly reported in a short conference proceeding by Lienhard et al. [181]. In the proceeding, they discovered an emitter in a 200 nm AlN epilayer that emits antibunched light with a ZPL at 2.08 eV (596 eV). No further investigation into AlN emitters was made until a number of papers a couple of years later [182], [183], including a manuscript discussed in this chapter in detail [184]. In these papers, AlN emitters were investigated at room and cryogenic temperatures that revealed quantum emission from individually addressable colour centres. The colour centres discovered by Lu et al. [181], [183] possess similar properties to emitters discussed in this chapter. However, Xue et al. [182] report on quantum emission from colour centres that span across the visible into the near-infrared, 560 to 960 nm.

3.2 Aluminium Nitride Quantum Emitters

Both GaN and AlN have large direct bandgaps, where the electronic bands are aligned at the Γ point in k-space, with a band gap energy $E_g$ of 3.4 and 6.2 eV respectively for their wurtzite phases. Both materials can host a number of atomic defects with energy states embedded within the band gap. For defect states that are located deep enough into the band gap, with an energy separation from the bulk states that is much greater than the thermal energy $k_B T$, carriers can be confined for timescales long enough to spontaneously emit a photon. This confinement can materialise in a number of ways. Three such confinement regimes are illustrated in Fig.3.1. In the figure, it is assumed only a single electron/hole is confined.

The first regime represents a defect state that is close to the conduction band of the material with an energy separation $E_d$. A number of different excitation and relaxation transitions are available. The electron can be excited from the valence band into the conduction band, using an excitation source with energy greater than the bandgap ($\geq E_g$). The electron preferentially relaxes into the

![Figure 3.1](image)

Figure 3.1: Defect energy states within a large band gap material. i) Defect energy state close to the conduction band, with a number of radiative and/or non-radiative transitions to and from the defect state. ii) Defect energy state close to the valence band. iii) Deep defect state embedded within the band gap, where the excited and ground state are separated from the bulk bands.
defect state via a radiative/non-radiative transition via emission of a photon(s)/phonon(s). For non-radiative relaxation into the defect state, a large number of phonons are created due to the maximum phonon energy in the order of 100 meV. The electron is confined in this location, crucially for a time long enough to enable spontaneous emission of a photon, as \( E_d \gg k_B T \). From this defect state the electron can relax to the valence band releasing a photon with a ZPL energy \( E_{ZPL} \approx E_g - E_d \), where \( E_{ZPL} \) is defined as the energy of the excited-to-ground state transition without emission/absorption of phonons. Conversely, the second regime in (ii) represents a defect state that is closer in energy to the valence band, where the ZPL transition is between the conduction band and the defect state. Here, a hole is confined at the defect ground state for long enough that a free electron within the conduction band can recombine into the hole and produce a photon with \( E_{ZPL} \approx E_g - E_v \). Both regimes represent red-shifted transitions that commonly occur in photoluminescence measurements for bulk materials with atomic impurities.

The third regime shown in Fig.3.1(iii) illustrates a defect state with two energy levels that are embedded within the band gap. Here, the defect comprises of both an excited \( |1\rangle \) and ground \( |0\rangle \) state which have an energy separation from the conduction and valence bands. These states can occur when complex impurities or a defect and a single impurity atom are situated within the lattice. If the energy difference between the conduction \( E_c \) (valence \( E_v \)) band and the excited (ground) state of the defect is greater than the thermal energy \( k_b T \), then an electron that is initially excited into the ground state via an excitation energy \( \geq E_v \) can get trapped into the two-level system. Here the system cycles between the ground and excited state, limited by the lifetime of the excited-to-ground state transition, via the application of sub-band gap optical excitation \( \geq E_{DS} \).

### 3.2.1 Confocal Imaging of AlN Quantum Emitters

To obtain an overview of the properties of emitters within AlN, a 1 \( \mu \)m AlN-on-sapphire epilayer was investigated using LSCM at room temperature. The unit cell and sample configuration is shown in Fig.3.2. A confocal scan map from the AlN sample is illustrated in Fig.3.2(iii). The scan map was taken at room temperature with a 532 nm continuous wave excitation source with optical filtering to measure the 550 to 650 nm spectral range. The filtering suppresses the strong fluorescence due to the Cr\(^{3+} \) chromium impurity common in sapphire epitaxial substrates. A spectral measurement showing the R1 and R2 fluorescent lines from sapphire can be found in the appendix in Fig.A.2. Localised emission spots from point-like emitters can be identified. Three emitters are labelled in the figure - AlN1 to AlN3. These defects are studied in detail within this chapter, and have been consistently relocated using a titanium (Ti) mask defined via a lift-off photolithography process. The metallic markers can be observed in the scan map. The density of the emitters is approximated to be 1.2 \( \mu \)m\(^{-2} \), which is sufficient for single emitter spectroscopy with a diffraction limited optical spot. The emitters were photo-stable over multiple measurements and multiple cooling cycles spanning over
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Figure 3.2: Sample structure and confocal scan maps of the AlN sample. i) Illustration of the unit cell of AlN in its thermodynamically favourable wurtzite phase. The polar c-plane axis [0001] is indicated. ii) Top down view of the unit cell, where all the semi-polar and non-polar facets are labelled. The c-plane is directed out of the page. iii) Confocal scan maps of the AlN substrate. Emitters of interest are labelled.

Figure 3.3: Spectral measurements of defects AlN1, AlN2 and AlN3 (i-iii) at room temperature. The ZPL and half maximum (HM) energies are labelled in each spectrum.

6 months.

3.2.2 Spectral Measurements

To obtain an understanding of the optical properties of the emitters at room temperature a number of spectral measurements were taken. The fluorescence from the background was accounted for by subtracting the background contribution from the defect emission by measuring the spectrum on and off an emitter. In some measurements, this contribution was completely corrected for and removed from the spectra. In a number of the spectra the background emission is still prevalent, as the AlN thickness is on the order of the axial resolution of the microscope. The spectral noise is ignored in Fig.3.3 using an axis break between 1.78 and 1.79 eV.

Figure 3.3 illustrates spectral measurements of emitters AlN1-3. There is a variation in spectral shape and intensity of the emission from the defects. The three spectra in Fig.3.3 demonstrate well defined ZPLs, the optical excited-to-ground state transition without coupling to optical phonons, labelled in
Chapter 3. Aluminium Nitride Quantum Emitters

the figure. A ZPL was not observable in every spectra of emitters in AlN, likely due to the intensity of the emission in the ZPL being too low, <1% the total intensity. In addition to the ZPL, the spectra illustrate coupling to phonons causing a greater than 0.4 eV broadening of the spectrum at room temperature due to the broad phonon side band (PSB) in each spectrum. In accordance with the Franck–Condon principle, the broadening on the low energy side of the ZPL is attributed to radiative transitions coupling to phonon modes via the creation of one or more phonons. Conversely, the high energy broadening is attributed to phonon assisted transitions via the absorption of phonons together with the photon. The asymmetric broadening around the ZPL materialises due to the lower probability of phonon absorption-assisted transitions due to their thermal occupation, and the high optical phonon energies in AlN up to 100 meV, four times the thermal energy $k_bT$ at room temperature. The room temperature ZPL linewidths for the three AlN emitters in Fig.3.2 are taken from fits to the spectra using Voigt functions with FWHM linewidths of $8.3 \pm 0.3$, $11.7 \pm 0.2$, and $9.4 \pm 0.2$ meV. The temperature-dependent broadening of the ZPL is explored in detail in Section 3.4. The ZPL contains 3.2% of the total intensity on average over the three spectra. The change in spectral shape between the emitters may result from their physical location in different strain fields or in proximity to other crystal dislocations and impurities.

To gain an understanding into the broadening of the spectrum of AlN1 a Raman scattering measurement is presented in Fig.3.4(b). The Raman measurement was taken on the same sample with a narrow linewidth 532 nm laser. The phonon energies available for Raman-active phonon modes within AlN can be determined from the Stokes-shifted Raman measurement. It is apparent that contributions from both the AlN and sapphire are observed in the measurement, as the thickness of the AlN epilayer is in the order of the axial PSF of the microscope. The determined Raman modes are labelled in the figure as determined from the literature [185], [186]. Using the relation $\Delta E = E_{ZPL} - E_{PX}$, where $E_{PX}$ is the peak energy for P1–P5 in Fig.3.4(i), it is possible to correlate the Raman shift due to the vibrational modes from the AlN with the peak locations. Ignoring the contributions due to vibrational modes from the sapphire, the Raman-shifted transitions $\Delta E$: $E_{2\text{LOW}}, A_{1\text{TO}}, E_{2\text{HIGH}}$ and $A_{1\text{LO}}$ are given as $31.2 \pm 0.1$, $76.7 \pm 0.3$, $81.70 \pm 0.01$, and $110.3 \pm 0.1$ meV, respectively. Therefore, one can hypothesise that the peaks P1 and P3 arise due to phonon assisted replicas from coupling to $E_{2\text{LOW}}$ and $E_{2\text{HIGH}}$, respectively, as well as peaks P2 and P5 from the corresponding two-phonon processes. In addition, P4 may be described by a mixed two phonon emission involving $E_{2\text{LOW}} + E_{2\text{HIGH}}$. In addition, the higher energy shifts are created by multi-phonon-assisted transitions. The phonon broadening can be understood considering the Franck–Condon principle.

The Franck–Condon principle provides a method for illustrating the interaction of a two-level system with phonons, quanta of lattice vibrations. According to the Franck–Condon principle, where an energy diagram is shown in Fig.3.5(i), electronic transitions, represented by vertical transitions such as the blue arrow, are instantaneous with respect to motion of the lattice. Due to the horizontal shift
Figure 3.4: Spectral properties of AlN quantum emitters. a) Spectral measurement of the emission from the emitter AlN1. The plot includes a histogram of 20 emitters ‘half maximum’ value, where the half maximum value corresponds to the energy at which each spectrum, on the higher energy side, has fallen to half its highest intensity. The half maximum value is illustrated in each spectrum in Fig. 3.3. b) Raman spectra from the AlN on sapphire substrate, taken with an excitation wavelength of 532 nm. Raman lines from both AlN and sapphire are observed in the measurements and are assigned to phonon modes using the green and blue colour, respectively.
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Figure 3.5: Formation of the phonon side band. i) Illustration of the Franck–Condon principle that governs the coupling to phonon modes via a quantum harmonic oscillator model, where the axis represents the configuration coordinate $q_i$ and energy $E$. ii) Energy level structure of the defect illustrating coupling to phonons in both emission and absorption. Phonon-assisted transitions are represented with a dashed arrow.

of the minimum (which represents the lattice distortion), transitions between different numbers of vibrational excitations are allowed. The X axis in the diagram represents the configuration coordinates $q_i$, where the subscript $i$ represents a particular vibrational mode of the lattice. The ground and excited lowest-vibrational states are labelled in the figure as $E_0$ and $E_1$, respectively. The probability of excitation from $E_0$ to a higher energy state via absorption of a photon is governed by the overlap integral of the states’ wavefunctions. In the figure, the most probable transition is the absorption of a photon with an energy equal to the ZPL energy $E_{ZPL} = E_0 - E_1$ and the energy of a single quantum of lattice vibration, $\hbar \Omega_i$. This is not the only allowed transition, as there is a finite probability of two or more quanta. From the excited vibration state $E_1 + \hbar \Omega_i$ the system relaxes down to the lowest energy excited state $E_1$ via the emission of a phonon with energy $\hbar \Omega_i$. Emission of a phonon is required to create a change in the configuration coordinates. From the excited state, photon emission mirrors absorption as the most probable transition is to a state one vibrational quanta higher in energy than $E_0$. The system again relaxes to the lowest-energy ground state $E_0$ via the propagation of the lattice vibration into the bulk. This leads to multiple allowed transitions with different energies and probabilities. Consider the spectra of AlN in Fig. 3.4(i). The phonon-assisted peaks P1 and P2 can be described in terms of the energy configuration diagram in Fig. 3.5(i) for the vibration mode $E_{2\text{LOW}}$, where $P1 \Rightarrow (E_1 - E_0) - \hbar \Omega_{E_{2\text{LOW}}}$ and $P2 \Rightarrow (E_1 - E_0) - 2 \times \hbar \Omega_{E_{2\text{LOW}}}$. Each of the aforementioned transitions are further broadened by acoustic-phonon assisted transitions and spectral wandering. The contributions therefore merge to form a single phonon band at ambient conditions.

In the illustration of the Franck–Condon principle in Fig.3.5(i) the vibronic modes of the lattice are modelled via a quantum harmonic oscillator. The oscillator strength and therefore probability of coupling to certain phonon modes is determined by the square of the vertical overlap of the modes’ wavefunction. The first approximation is that the oscillator potential is equal in both states, as the curvature of the potential wells are the same. The second assumption is the so called low temperature
assumption: only the lowest-energy vibronic mode is excited in absorption. At ambient temperatures, thermal energy may promote the system to vibronic modes energetically higher than $E_0$ and $E_1$, which may lead to radiative transitions with an energy higher than $E_{ZPL}$. The lowest energy optical phonon mode in the Stokes-shifted Raman measurement in Fig.3.4(ii) is $E_{2\text{LOW}} = 31.2 \pm 0.1$ meV. Considering the thermal energy $k_B T = 26$ meV at room temperature, it is apparent that the thermal energy is insufficiency to excite the $E_{2\text{LOW}}$ mode. This suppresses the probability of photon-absorption assisted transitions and determines why no high energy phonon replicas were observed in spectra of AlN emitters.

Whilst the electronic transition in the Franck–Condon principle is said to be instantaneous, there is a finite lifetime associated with the decay of the excited state as the state spontaneously emits a photon with a constant probability, leading to an exponential decay of the state and thus the emission. The natural line shape of a purely electronic transition with no coupling to phonons is Lorentzian with a linewidth determined by the Heisenberg uncertainty principle: an uncertainty in time of the occupation of the excited state leads to an uncertainty in energy of the excited state. The coupling to acoustic and optical phonon modes act to broaden the natural linewidth in accordance with the Franck–Condon principle.

The optical properties of the emitters in AlN were investigated in more detail by measuring the spectra of 20 emitters. The spectrum of AlN1 in Fig.3.4(i) shows a well defined ZPL, which however was not observed for every emitter. In order to build a statistical picture of the distribution of emission wavelengths in AlN, a half maximum (HM) value was defined. This value corresponds to the energy at which the spectrum, on the higher energy side, has fallen to half its highest intensity. The HM value for AlN1-3 is illustrated in Fig.3.3. The HM value was used to create the histogram of emission energies presented in Fig.3.4 where the axis representing the number of emitters in each bin of the histogram is on the right hand side of the plot. The bin width for the histogram is 50 meV. The histogram illustrates that the majority of the emitters have their HM between 2.1 and 2.25 eV, corresponding to ZPLs between 2.00 and 2.15 eV. This represents a smaller spectral distribution as compared to colour centres reported in GaN, where the ZPL energy between emitters within the same sample varies over 0.4 eV [176]. The smaller variation in the ZPL energy for these AlN emitters provides an advantage for their exploitation in photonic and/or optoelectronic devices coupled to narrow-band cavities or antennae. In addition, it suggests a common origin for all the emitters observed in AlN, with energy shifts between emitters resulting from differences in strain, local dislocation density, impurities, and/or point defects.

In addition to broadening due to interactions with lattice vibrations, nearby charge traps in the form of other defects and/or impurities can cause a Stark shift in the energy of the ZPL due to the formation of a finite localised electric field in proximity to the defect. This is often referred to as spectral wandering or spectral diffusion. The short timescales that charges are trapped for requires photon
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Figure 3.6: AlN emitter absorption and emission polarisation characteristics. i) Emission and absorption polarisation measurements for an emitter in AlN. ii) Statistical analysis of the absorption dipole angle for a number of emitters in AlN, with (blue) and without (green) filtering of the measurement from the histogram due to the fit parameters.

3.2.3 Polarisation-Resolved Spectroscopy

An important consideration for single photon emitters is the polarisation of the emission. Ideally, each photon will have the same polarisation. To investigate the polarisation properties of emitters in AlN polarisation optics are included in the microscope as shown in Chapter 2 in Fig. 2.1. Measurement of the absorption polarisation was achieved by rotating the laser polarisation using a half wave plate (HWP). The polarisation of the collected fluorescence was measured using a thin-film linear polariser with a 1000:1 extinction ratio. An absorption and emission measurement is shown in the polar plot in Fig. 3.6 (i). The absorption and emission polarisation follows that of a single dipole orientated close to the plane of the sample. The polarisation measurements were fit using a dipole emission pattern with the polar in-plane angle $\theta$ and the azimuthal out-of-plane angle $\phi$ in the following form [187],

$$I(\theta, \phi) = \zeta (1 - \sin^2(\theta) \cos^2(\phi)),$$

where $\zeta$ is a normalisation factor. A fit to an absorption (blue circles) and an emission (green triangles) measurement of AlN1 is shown in Fig. 3.6 (i). The emission dipole has an extinction ratio defined by $I_{\text{Max}} / I_{\text{Min}}$ of 74:1. This illustrated predominantly in-plane emission with a small azimuthal angle taken from the fit $\phi = 8.0 \pm 0.5^\circ$. The absorption measurement has an extinction ratio of 6.7:1 with an azimuthal angle $25.8 \pm 0.4^\circ$. There is a $91.4 \pm 0.3^\circ$ change in polar angle between the excitation and absorption dipoles. An angular discrepancy between the absorption and emission dipoles have been reported before for emitters in GaN [177], h-BN [96], [188] and diamond [189].

The finite angular difference between emitters absorption and emission dipoles may have multiple physical origins. Exarhos et.al. [188] discuss the possibility of dipole reorientation between different...
atomic configurations causing the finite angular shift in dipole orientation, something they suggest is unlikely for crystalline materials at room temperature. Stable photoemission over long enough timescales to measure the absorption/emission dipole, producing high polarisation extinction ratios as seen for the GaN/AlN emitters in Fig.3.6 suggests that atomic reconfiguration is unlikely as any reconfiguration would have to be stable/reproducible to measure said extinction ratios. The presence of multiple excited states, with different polarisation selection rules, could lead to a cascade transition from a higher energy excited state to an orthogonal lower energy excited state. Further information with regards to the energy level dynamics of the emitters is investigated in this chapter using time-correlated photon counting measurements, where an energy level system with four levels is hypothesised to account for the orthogonal absorption and emission dipoles.

The absorption polarisation properties of over 400 emitters, measured for a subsequent experiment in Chapter 5, is illustrated in Fig.3.6(ii). Over the 400 sampled emitters no trend in the polar angle and alignment of the absorption dipoles can be observed. Filtering the emitters by excluding polarisation measurements with a goodness of fit value $R^2 < 0.7$ results in 82 polarisation absorption measurements. These measurements are binned and illustrated in the histogram as the green bars. The data is not sufficient to draw any conclusion as to the alignment of the emitters’ dipole with the crystal orientation. One would expect a 60° delta between the dipoles due to the tetrahedral configuration of the unit cell.

### 3.3 Time-Correlated Single Photon Counting

Time-correlated single photon counting (TCSPC) measurements reveal the lifetime and quantum nature of the fluorescence from an emitter. In this subsection, TCSPC measurements are used to investigate the underlying energy level structure of AlN emitters in detail. We begin our analysis by considering a two-level system using rate equations.

#### 3.3.1 Rate Equations : Two Level Model

The least complex electronic energy-level model to describe a quantum emitter is a two-energy level model. At room temperature, where strong interactions with the environment lead to fast coherence decay between the excited and ground states, one can model the system as a non-resonantly pumped dipole emitter with energetically relaxed and excited states. The energy difference between the relaxed and excited states, $|0\rangle$ and $|1\rangle$ respectively, is given by $\hbar\omega_0$. The system is pumped with an excitation source, typically a monochromatic laser, with energy $\hbar\omega_1 > \hbar\omega_0$. Upon absorption of a photon, the system is excited from the $|0\rangle$ state to a vibronic state energetically higher than the excited state of the system. The system relaxes from the vibronic state to the excited state on picosecond timescales via the creation of vibronic modes in the crystal. The system can then spontaneously emit a photon.
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with frequency $\omega_0$ via the electronic transition $|1\rangle$ to $|0\rangle$. From the ground state, the carrier is re-excited into the excited state via absorption of another photon, cycling the spontaneous emission of photons. Under the assumptions that the system is non-resonantly driven, with a pump rate $k_{01}$ that is proportional to the intensity of the pump, and that all vibronic interactions are much faster than the spontaneous emission lifetime of the system, one can use rate equations to describe the population dynamics of the system,

$$\begin{bmatrix} \dot{p}_0 \\ \dot{p}_1 \end{bmatrix} = \begin{bmatrix} -k_{01} & k_{10} \\ k_{01} & -k_{10} \end{bmatrix} \begin{bmatrix} p_0 \\ p_1 \end{bmatrix},$$  \hspace{1cm} (3.2)

As carriers must be found in either the excited or relaxed states, as assumed in this model, the populations $p_0$ and $p_1$ satisfy $p_0 + p_1 = 1$. In addition, with continuous wave laser excitation, the system reaches equilibrium where $\dot{p}_0 = \dot{p}_1 = 0$. Under the equilibrium condition, one can solve the rate equations for the excited state yielding,

$$p_1(\infty) = \frac{k_{01}}{k_{01} + k_{10}},$$  \hspace{1cm} (3.3)

which follows a saturating behaviour. Rewriting the second order correlation function in terms of annihilation and creation operators and using quantum regression theorem one can arrive at the well known function for the second order correlation function of a two-level system [190],

$$g^{(2)}(\tau) = 1 - e^{-|\tau|/\tau_0},$$  \hspace{1cm} (3.4)

where,

$$\tau_0 = \frac{1}{k_{01} + k_{10}}.$$  \hspace{1cm} (3.5)

3.3.2 Photon Emission Rate From a Single Dipole

It is assumed for the two-level model that the excitation rate from the ground $|0\rangle$ to the excited state $|1\rangle$ is proportional to the intensity of the pump. The pump rate $k_{01}$ is given as,

$$k_{01} \propto aP_e,$$  \hspace{1cm} (3.6)

where $a$ is a constant and $P_e$ is the pump power. As the emission of photons from the two-level system is governed by the population of the excited state, the photon emission rate can be determined using the steady state population of $|1\rangle$ given in Eq 3.3. The photon emission rate $\Gamma$ is equal to the product of the rate of decay from the excited state $k_{10}$, which is the inverse of the excited state lifetime $\tau_{10}$, and the population of the excited state $p_1$. Thus, the photon emission rate can be expressed at equilibrium
in terms of the pump rate using Eq.3.3 and Eq.3.6 as,

\[ \Gamma(P_e) = k_{10}p_1(\infty) = \frac{k_{10}P_e}{P_e + k_{01}/a} = \frac{I_\infty P_e}{P_e + P_{\text{sat}}}, \quad (3.7) \]

with a constant \( P_{\text{sat}} = k_{01}/a \). An additional term can be included, \( \beta P_e \), which represents any background emission from the substrate that is assumed to be linearly dependent on the pump power.

\[ \Gamma(P_e) = \frac{I_\infty P_e}{P_e + P_{\text{sat}}} + \beta P_e. \quad (3.8) \]

The photon emission rate follows a saturation behaviour, tending towards an intensity \( I_\infty \propto k_{10} \) for excitation powers larger than the constant \( P_{\text{sat}} \). A power-dependent intensity measurement taken on an emitter in AlN demonstrates the saturating nature of photo emission and is shown in Fig.3.7(i), along with an illustration of the two-level energy model (iii). The background fluorescence from a location next to the emitter is subtracted from the measurement. The power-dependent fluorescence measurement demonstrates a clear saturation of the emission intensity at high pump powers, suggesting a single if not small number of emitters in the optical PSF. Eq.3.7 is used to fit the data, with a saturation intensity \( I_\infty = 310 \pm 10 \text{ kcps} \). The saturation power \( P_{\text{sat}} = 1.4 \pm 0.1 \text{ mW} \) is determined from the fit. The excitation pump power needed to saturate the emitter is comparable to other wide band gap emitters such as in diamond and silicon carbide [180].

### 3.3.3 Second Order Correlation of Light

The quantum nature of the light from an emitter can be quantified by probing the photon statistics using a Hanbury Brown and Twiss interferometer. The experimental setup is discussed in detail in Chapter 2. A second order correlation measurement of emitter AlN1, taken with a pump power
$P = 30\mu W$ where $P/P_{sat} = 0.02$, is shown in Fig.3.7(ii). The measurement was taken with optical filtering to select the 550 to 650 nm spectral range. The absence of correlations around time zero illustrates the anti-bunched nature of the light. The data between $\pm(38 - 45 \text{ ns})$ is removed from the plot to ignore optical interference between the detectors. A fit to the data is shown in the figure using an adaptation of Eq.3.4 that includes the background fluorescence in the following form [172],

$$g^{(2)}(\tau) = 1 - P_f^2 + P_f^2(1 - e^{-|\tau|/\tau_0}),$$

(3.9)

where $P_f$ is the probability that a detection event occurs due to the fluorescence from an emitter. The probability from the fit is given as $P_f = 0.9$. The fit to the data illustrates the two-level nature of the emission. The raw data is corrected for the background fluorescence using unbalanced detector count rates, as discussed in Chapter 2.2.3.1. The signal rates on the two detectors were 4700 and 3750 cps with unbalanced dark counts of 50 and 520 cps. The corrected data is shown in the figure with the empty symbols. The background correction accounts for the Poissonian contribution from the background with $g^{(2)}(0) = 0.06$, illustrating the single photon purity of the source at low pump powers. The two-level model is adequate at describing the photon statistics at low pump power. However, pump power-dependent measurements suggest the presence of a more complicated energy level structure with the emergence of a bunching at high pump powers.

The pump power-dependent second-order correlation of the photon stream from an AlN emitter, post-processed from time tagged photon arrival data, is presented in Fig.3.8. The data between $\pm(8 \rightarrow 30 \text{ ns})$ is ignored due to the contributions from optical cross-talk between the detectors. Antibunching is observed at time zero, where no photons arrive on both detectors simultaneously. The inset in (i) focuses on the antibunching revealing a power-dependent antibunching time. The occurrence of bunching at higher pump power hints at the desheling of the system into a metastable state, often seen in other solid state emitters such as the NV centre in diamond [110], [111], [113]. It is clear from the previous analysis for a two-level system that the function derived in Eq.3.4 is not adequate to describe the power-dependent bunching. A three-level model with a power-dependent desheling to the metastable state is considered, as illustrated in Fig.3.8(ii).

### 3.3.4 Rate Equations : Three Level Model

In order to account for the pump-power-dependent bunching statistics observed in Fig.3.8, a third energy level is included in the model. The additional energy level, often referred to as a shelving or metastable state, retains carriers on lifetimes greater than the lifetime of spontaneous emission. Assuming the shelving state depopulates via a non-radiative transition to the ground state, photon emission is suppressed. The ‘on’ and ‘off’ dynamics results in a bunching effect in the photon statistics. The rate equations for a three-level system illustrated in Fig.3.8(ii) are in the form,
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Figure 3.8: Power dependent second-order correlation measurements. i) $g^{(2)}(\tau)$ measurement with increasing pump power, demonstrating strong antibunching photon statistics as well as a power-dependent bunching. The measurements are vertically offset by 2 for clarity. ii) Three level energy level model used to describe the occurrence of photon bunching at high pump powers.

\[
\begin{bmatrix}
\dot{p}_0 \\
\dot{p}_1 \\
\dot{p}_2
\end{bmatrix} =
\begin{bmatrix}
-k_{01} & k_{10} & k_{20} \\
k_{01} & -(k_{10} + k_{12}) & 0 \\
0 & k_{12} & -k_{20}
\end{bmatrix}
\begin{bmatrix}
p_0 \\
p_1 \\
p_2
\end{bmatrix},
\]

(3.10)

and $p_1 + p_2 + p_3 = 1$. The rate equations can be solved analytically, again for the population of interest, the excited state population at equilibrium [113]:

\[
p_1(\infty) = \frac{k_{01}}{(1 + \frac{k_{12}}{k_{20}})k_{01} + k_{10} + k_{12}}.
\]

(3.11)

Using a similar analysis as for the two-level system, one can arrive at the second order correlation function for a three-level system [110, 189, 191],

\[
g^{(2)}(\tau) = 1 - (1 + \alpha)e^{-\frac{\tau}{\tau_1}} + \alpha e^{-\frac{\tau}{\tau_2}},
\]

(3.12)

\[
\alpha = \frac{1 - \tau_1 k_{20}}{k_{20}(\tau_2 - \tau_1)} \quad \text{and,} \quad \tau_{1,2} = \frac{2}{A \pm \sqrt{A^2 - 4B}},
\]

(3.13)

where,

\[
A = k_{01} + k_{10} + k_{12} + k_{20} \quad \text{and,} \quad B = k_{01}k_{12} + k_{01}k_{20} + k_{10}k_{20} + k_{12}k_{20}.
\]

(3.14)

The power-dependent photon emission rate, $\Gamma(P_e)$, can be derived for a three-level system again considering the excited state population at equilibrium assuming a linear dependence between the pump power and the transition rate $k_{01}$.
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\[ \Gamma(P_e) = k_{10}P_1(\infty) = \frac{\zeta k_{10}P_e}{P_e + P_{sat}}, \]  

(3.15)

with,

\[ \zeta = \frac{1}{1 + \frac{k_{12}}{k_{20}}} \quad \text{and} \quad P_{sat} = \frac{\zeta(k_{10} + k_{12})}{a}. \]  

(3.16)

These lengthy expressions do not present much intuition with regards to the impact of the shelving of carriers on the photon emission rate. For clarity regarding the impact of the shelving one can define the source efficiency, \( \eta_s \), for both the two-level and three-level models,

\[ \eta_s = \Gamma(P_e = \infty), \]  

(3.17)

which for the two-level and three-level models respectively results in the pump independent source efficiency of,

\[ \eta_s = k_{10} \quad \text{and} \quad \eta_s = k_{10}\zeta = k_{10}\left(\frac{1}{1 + \frac{k_{12}}{k_{20}}}\right). \]  

(3.18)

One can observe that, for a negligible shelving rate \( k_{12} \ll k_{10} \), the three-level model approaches the efficiency of the two-level system. However, even a small shelving rate, where the carrier is shelved for a significant timescale such that \( k_{12} \gg k_{20} \), can have a drastic impact on the source efficiency and the photon emission rate. The shelving of the system can be understood by considering the system as being in an ‘on’ and ‘off’ state, where upon population of the excited state the system is ‘on’ and able to emit photons. The existence of the shelving state, where the system is ‘off’, leads to additional fluctuations in the fluorescence intensity. This is observed as a bunching of the photon statistics over long timescales, as is apparent in Fig.3.8. To understand the exact dynamics that leads to the antibunching/bunching timescales two three-level models are investigated, the first that considers a pump power-independent deshelving of \(|2\rangle\) and the second a pump-dependent deshelving.

### 3.3.5 Three Level Model : Power Independent Deshelving

In the first model, the deshelving rate, \( k_{20} \), was assumed to be independent of the pump power. In addition to \( k_{20} \), the rates \( k_{10} \) and \( k_{12} \) are constant and were determined from the fit parameters \( \alpha, \tau_1 \) and \( \tau_2 \) at vanishing powers in the following manner [190]–[192],

\[ k_{20} = \frac{1}{(a + \alpha^\infty)\tau_2^\infty}, \]  

(3.19)

\[ k_{12} = k_{20}\alpha^\infty, \]  

(3.20)
\[ k_{10} = \frac{1}{\tau_1^0} - k_{12}. \]  

(3.21)

Where the superscripts \( \infty \) and 0 represents the values at infinite and zero pump power respectively. For the models, these values were taken as the values at the lowest (4 \( \mu \)W) and highest (800 \( \mu \)W) pump power. The pump rate \( k_{01} \) was assumed to be linearly dependent on the pump power,

\[ k_{01} = \sigma P \text{ and } \sigma = \frac{k_{12}k_{20} + k_{10}k_{20}}{(k_{12} + k_{20})P_{\text{sat}}}, \]  

(3.22)

where \( \sigma \) is the absorption cross-section of the dipole and \( P_{\text{sat}} \) was determined from the fit to a power-dependent saturation measurement in Fig.3.9(iv) using Eq.3.8 where \( P_{\text{sat}} = 12.5 \pm 0.5 \mu \text{W and } I_\infty = 670 \pm 5 \text{kcps.} \) The best fit to the data was achieved using a finite \( \beta \) value in the fit, with \( \beta = 134 \pm 9 \text{kcps/mW.} \) The data was taken for an emitter under a solid immersion lens (SIL), as discussed in detail in Chapter 5. The fit parameters at vanishing powers are given as; \( \tau_1^0 = 4.6, \) \( \tau_2^0 = 1100, \) \( \tau_1^\infty = 52 \text{ns and } \alpha^\infty = 3.3, \) resulting in the static rates for the various transitions; \( k_{20} = 2.96, \) \( k_{12} = 10.37 \) and \( k_{10} = 218.39 \text{MHz.} \) The resultant power-dependent parameters from the model are shown in Fig.3.9 with the blue solid line.

It is apparent from Fig.3.9(i-iii) that the power-independent desheling does not accurately predict the transition dynamics of the emitter as determined from the power-dependent second-order correlation measurement. The bunching parameter, \( \alpha, \) presents the best fit to the data where the general trend of the saturating bunching parameter is determined. However, the model does not describe the antibunching and bunching lifetimes \( \tau_1 \) and \( \tau_2. \) A divergence from the data for \( \tau_1 \) is observed, however the general exponential trend is followed. For \( \tau_2 \) the trend is not observed, especially at lower pump powers. This has been observed before in the literature and is often attributed to a a power-dependent desheling of |2⟩ back to the excited state |1⟩ \[191], [192]. Therefore, the power-dependent desheling is accounted for in the following model.

### 3.3.6 Three Level Model : Power Dependent Desheling

In order to account for the power-dependent desheling an alternative set of rates are derived for the transition, as presented in the literature [191], [192]. The contribution of a power-dependent desheling is justified due to the expectation that a linearly dependent desheling rate would result in \( \alpha^\infty = 0 \) and \( \tau_2^\infty = 0, \) which is not consistent with the dataset in Fig.3.9. The modification to the previous model is made by modifying the desheling rate \( k_{20} \) to follow a saturating law in the following manner,

\[ k_{20} = \frac{dP}{P + c} + k_{20}^0, \]  

(3.23)
Figure 3.9: Power-dependent fit parameters for transition rate modelling. Fit parameters $\alpha$ (i), $\tau_1$ (ii) and $\tau_2$ (iii) for the power-dependent second order correlation measurements in Fig. 3.8. The two lines represent the model parameter values, where the blue solid line represents the power-independent deshelving of the metastable state and the red dashed line the improved power-dependent deshelving model. iv) Saturation measurement from the same emitter as (i-iii). v) Three level energy model with a power-dependent deshelving of the metastable state.
with,

\[ k_{20}^0 = \frac{1}{\tau_2^2} \quad \text{and} \quad d = \frac{\frac{1}{\tau_2^2} - (1 - \alpha^\infty) \frac{1}{\tau_2^2}}{\alpha^\infty + 1}, \]  
(3.24)

\[ k_{12} = \frac{1}{\tau_2^2} - k_{20}^0 - d \quad \text{and} \quad k_{10} = \frac{1}{\tau_1^2} - k_{12} \]  
(3.25)

For the new model, only \( k_{12} \) and \( k_{10} \) are power-independent. Using the parameters at vanishing powers, \( k_{12} = 10.3 \) and \( k_{10} = 214 \text{ MHz} \). The absorption cross section \( \sigma \), and thus \( k_{01} = \sigma P \), can no longer be approximated by the saturation power. \( \sigma \) is determined from a fit to \( \tau_1 \) using Eq.3.13 as the antibunching lifetime is unaffected by the desheling rate \( k_{20} \). The final undetermined rate \( k_{20} \) is approximated by the free parameter \( c \) by a fit to the bunching parameter \( \alpha \). The resultant model is shown in Fig.3.9 as the dashed red line. The applicability of the model is determined from \( \tau_2 \), where an improvement in matching the experimental data is observed, especially at lower pump powers. However, the model still fails to accurately determine the bunching parameters, suggesting that the exact transition dynamics of the system are better described by a more complex model.

### 3.3.7 Hypothesised Four Level Model

The analysis thus far has assumed fixed polarisation in the dynamics. The cross-polarised emission and absorption measurement in Fig.3.6(i) can be incorporated in the model by considering the four-level energy level structure highlighted in the dashed box in Fig.3.10(i). In this configuration, the following transitions lead to antibunched photon statistics. The system is initially prepared into the horizontally polarised ground state, \( |H_0 \rangle \). The electron is excited to the horizontal excited state \( |H_1 \rangle \) by absorption of a photon. The electron preferentially relaxes to the vertically polarised excited state \( |V_1 \rangle \) via a non-radiative transition. From \( |V_1 \rangle \), the system decays to the ground state \( |V_0 \rangle \) by emission of a vertically polarised photon. Ultimately, the population decays back to the \( |H_0 \rangle \) state, where the cycle can repeat. The described transitions explain the cross-polarised absorption and emission dipoles observed in the measurement.

To incorporate the power-dependent bunching of the photon statistics in the four level model one can include a metastable shelving state as previously discussed for the three level model. The four level model with the shelving state is shown in Fig.3.10(i). However, considering the cross-polarised dipoles, one could explain the bunching considering the four-level model as shown in (ii). In this model, the bunching is considered by assuming that the transition rate of the vertical dipole \( k_V \) is much faster than the transition rate of the horizontal dipole \( k_H \). At low pump powers, the electron follows the aforementioned transitions to only emit vertically polarised photons. At higher pump powers, the population of the \( |V_1 \rangle \) transfer to \( |H_1 \rangle \) via excitation to a vibrational state. As the transition rate is much slower than the vertical dipole, the carrier is trapped at this location on timescales much
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Figure 3.10: Hypothesised four level energy level model for AlN quantum emitters. i) Four level energy model with cross-polarised dipoles labelled in the gray dashed box. A power-dependent desheling to a higher energy vibrational state illustrates the occurrence of bunching in the photon statistics at high pump power. ii) Illustration of an additional hypothesised desheling from the lower energy $|V_1\rangle$ excited state to the higher energy $|H_1\rangle$ state.

longer than the emission timescales of the vertical dipole. This leads to a power-dependent bunching of the photon statistics in a manner similar to the shelving of carriers in a metastable state. In the future, one could uncloak the exact dynamics with polarisation resolved power-dependent spectral and photon counting measurements.

3.4 Temperature Dependent Spectroscopy

Low temperature spectroscopy enables investigation of the photo-physical properties of emitters by probing their energy structures whilst limiting phonon interactions. In this subsection, the low temperature and temperature dependent properties of the emitter AlN1 are discussed.

Figure 3.11: Temperature dependent spectroscopy of the AlN1 quantum emitter in AlN. i) Spectral measurements taken at 4K showing the reduced linewidth of the ZPL. ii) Temperature dependence of the ZPL centre energy and FWHM linewidth. iii) Second-order correlation measurement at 4K, demonstrating clear bunching and antibunching photon statistics.
A spectral measurement taken at 4 K is presented in Fig. 3.11(i). A narrowing of the ZPL linewidth is observed, due to the limited interactions with phonon modes in the semiconductor. The measured FWHM linewidth at 4 K, $\Delta w_V = 0.71 \pm 0.01$ nm, is 5 times smaller than the room temperature ZPL. The linewidth is derived from a fit to the spectrum in Fig. 3.11(i) with a Voigt function. The Voigt function is a convolution of a Gaussian function with a FWHM $w_G$ and a Lorentzian with a FWHM $w_L$ in the following form,

$$I_V(\lambda) = I_0 + \frac{2A}{\pi^{1/2}} \frac{w_L}{w_G} \int_{-\infty}^{\infty} \left( \frac{\ln(2) \frac{w_L}{w_G}}{\sqrt{\ln(2) \frac{w_L}{w_G}}} \right)^2 + \left( \sqrt{4 \ln(2) \frac{\lambda - \lambda_0}{w_G} - t} \right)^2 dt',$$  

(3.26)

where $\lambda_0$ is the wavelength at the centre of the Gaussian and Lorentzian and $t'$ is a dummy variable for the integration. The FWHM of the Voigt function is approximately 0.5346 $w_L + \sqrt{0.2166 w_L^2 + w_G^2}$.  

(3.27)

The expression for $w_V$ approximates the FWHM with a 0.02 % accuracy [193]. The measured linewidth is three times larger than the approximate resolution of the spectrometer with a FWHM $\Delta \lambda = 0.23$ nm. Spectral measurements taken from 4 to 300 K are presented in Fig. 3.11(ii). A low temperature second order correlation measurement, shown in Fig. 3.11(iii), illustrates the presence of bunching as well as antibunching at low temperatures. The occurrence of bunching at low temperature in the measurement suggests that shelving of the carriers at high pump power is independent of temperature. The temperature $T$ dependent linewidth $w_V$ follows a Bose-activated broadening from 10 to 300 K as described by,

$$\Delta \gamma_{\text{FWHM}} = \gamma_0 + \frac{\beta}{e^{E/k_B T} - 1},$$  

(3.28)

where $\gamma_0$ represents a temperature-independent broadening, i.e. spectral wandering, $\beta$ is a coupling coefficient and $E$ is an activation energy. A good fit to the data is achieved with the parameters; $\gamma_0 = 2.90 \pm 0.04$ meV, $\beta = 29.7 \pm 0.4$ meV, and $E = 52.0 \pm 0.3$ meV. The activation energy does not correspond to any of the Raman active phonon energies measured in Fig. 3.4(ii) or any other known optical phonon energies in AlN. To understand the temperature dependent broadening of the ZPL, contributions due to both homogeneous and inhomogeneous broadening are considering in the following manner.

The spectral shape of an optical transition is governed by both homogeneous and inhomogeneous broadening mechanisms. The difference between homogeneous and inhomogeneous broadening can be understood by considering the local environment surrounding an emitter. Any broadening mechanism that is dependent on the surrounding environment is said to be inhomogeneous. An example of an inhomogeneous broadening mechanism is that of an oscillating charge trap in proximity to an emitter.
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Figure 3.12: Voigt fitting of the ZPL line shape for the emitter AlN1. i) Spectral measurements of the ZPL at 10K fit with a Gaussian (blue, solid line) and Lorentzian (green, dashed line) function. ii) Temperature dependence of the FWHM width of the ZPL of AlN1. The Gaussian (blue, triangle) and Lorentzian (green, circle) FWHM is extracted from a Voigt fit to the ZPL.

The change in local electric field introduces a Stark shift and a spectral wandering of the transition energy. In contrast, a homogeneous broadening mechanism is one that impacts each emitter in the same manner. An example is lifetime or natural broadening, where the line shape is broadened due to the uncertainty of the excited state population and the finite lifetime of the optical transition. The natural linewidth is governed by the lifetime $\tau$ in the following manner,

$$\Delta E \approx \frac{\hbar}{2\pi \Delta \tau} = \frac{\hbar}{\tau_{10}}. \quad (3.29)$$

Consider the antibunching lifetime $\tau_0 = 1/(k_{01} + k_{10})$ for a two level model. At vanishing pump power the lifetime is dependent only on the rate $k_{10}$. Therefore, the antibunching lifetime at zero pump power represents the spontaneous emission lifetime $\tau_{10}$ for a two level model. Considering that the photon statistics at low pump power are well described by a two-level model, one can use the antibunching lifetime $\tau_0$ to extrapolate $\tau_{10}$ from fits to power-dependent second order correlation measurements. The extrapolated lifetime for the fit to the data in Fig.3.9 presents $\tau_{10} = 4.6 \text{ ns}$. This represents a natural broadening $\Delta E \approx 0.14 \mu \text{eV}$. The observed broadening is therefore four orders of magnitude greater than the natural broadening. It is clear that additional broadening mechanisms act to increase the linewidth at low temperatures.

Phonon broadening is also considered homogeneous. Over a number of measurements the impact of phonons averages between emitters and follows a Lorentzian broadening of the ZPL. To independently investigate the inhomogeneous (spectral wandering) and homogeneous (phonon) broadening of the ZPL the Voigt function in Eq.3.26 can be fitted to the temperature dependent line shape in accordance with the literature [194], [195]. This enables extrapolation of the Gaussian and Lorentzian linewidth from a single fitted function. The temperature dependence of the ZPL FWHM is investigated in more detail in Fig.3.12.

A spectrum of the ZPL at 10K is shown in Fig.3.12(i). The spectrum was fit with a Gaussian and a
Lorentzian function, shown in the plot as the blue solid line and green dashed line, respectively. The best fit to the data was achieved using a Gaussian function, indicating that the ZPL is broadened at low temperature by an inhomogeneous process. The broadening is attributed to fast spectral wandering of the ZPL. The temperature dependence of the ZPL linewidth is investigated in (ii). The temperature dependent ZPL line shape was fit using the Voigt function in Eq. 3.26. The Gaussian $w_G$ and Lorentzian $w_L$ FWHM is shown in Fig. 3.12(ii) as a function of the temperature. The data demonstrates a temperature dependence on the broadening. At low temperatures, the ZPL is Gaussian, with $w_G = 3.29 \pm 0.04$ meV and $w_L \approx 0 \left(10^{-17} \text{eV}\right)$ at 10 K. Conversely, at temperatures above 100 K the lineshape is best described by a Lorentzian function, with $w_L = 6 \pm 1$ meV and $w_G \approx 0 \left(10^{-8} \text{eV}\right)$ at 200 K.

The Lorentzian line shape of the ZPL at high temperatures indicates a homogeneous broadening due to phonons. The temperature at which the phonon broadening starts to dominate over the inhomogeneous broadening can be determined by fitting $w_G$ and $w_L$ with the Bose-activated function in Eq. 3.28. The deactivation and activation energy for the inhomogeneous $E_i$ and homogeneous $E_h$, respectively, is extracted from the fit and given as $E_i = 30 \pm 10$ and $E_h = 36 \pm 5$ meV. The uncertainty of the fit materialises due to the lower probability of non-phonon assisted ZPL transitions at high temperatures. Interestingly, the deactivation and activation energies $E_i$ and $E_h$ correspond to the energy of the $E_{2\text{LOW}}$ Raman-active phonon mode, as determined in the Stokes-shifted Raman measurement in Fig. 3.4(ii), where $E_{E_{2\text{LOW}}} = 31.2 \pm 0.1$ meV. The temperature dependent broadening of the ZPL can be understood considering the following. At low temperatures, the broadening is attributed to spectral wandering of the ZPL. Limited phonon interactions result in a line shape that is predominantly Gaussian due to the inhomogeneous spectral wandering of the ZPL line. As the temperature increased, interactions with the $E_{2\text{LOW}}$ phonon act to broaden the linewidth. At temperatures above 200 K the broadening is dominated by the homogeneous phonon interactions. The inhomogeneous spectral wandering is investigated in more detail in Fig. 3.13.

To probe the spectral wandering further time-dependent spectra are taken with an integration time of 2 s. The time-dependent spectra are presented in a heatmap in Fig. 3.13(i). On observation, the ZPL appears stable over integration time of 2 s for each measurement. Fits to each spectrum using a Gaussian function reveals instability. The time-dependent change in ZPL centre wavelength $\Delta \lambda_{ZPL}$ and FWHM linewidth is illustrated in Fig. 3.13(ii) and (iii) respectively. A wandering $< \pm 0.1$ nm is observed around the mean centre wavelength. The greatest absolute drift from the mean is 0.09 nm. The time-dependence of the linewidth is shown in (iii). The spectral wandering of the ZPL leads to a variation in the linewidth observable in the plot. The mean linewidth is $0.23 \pm 0.03$ nm with a maximum and minimum of 0.13 and 0.36 nm respectively. The reported linewidth is 3 times smaller than the linewidth extracted in Fig. 3.11(i), likely due to the lower excitation power and faster integration time used for the measurements. To probe the spectral wandering on $< 2$ s timescales,
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Figure 3.13: Time-resolved spectral measurements of emitter AlN1. i) Time-resolved spectra taken every two seconds for 26 minutes. ii) ZPL wavelength extracted from a Gaussian fit to each spectra in i). The shaded area represents the error. iii) Linewidth of the optical transition as a function of time.

3.5 Conclusion and Future Outlook

Whilst a significant amount of information was uncovered with regards to the photon emission properties of AlN emitters, additional information is required to reveal the physical origin of the emission. Polarisation-resolved photoluminescence excitation (PLE) measurements, where the frequency of a sharp-linewidth excitation source is varied, would facilitate measuring in more detail the absorption properties of the emitters, potentially presenting a more complete picture of the energy level structure. In addition, the spin properties of the emitter may be probed by techniques such as optically detected magnetic resonance (ODMR) and electron paramagnetic resonance (EPR), where the spin of the electron may be investigated to be used as a spin qubit. It is worth noting that, due to the non-zero nuclear spins of aluminium and nitrogen, AlN may not present the ideal environment for spin-based quantum photonic technologies, as de-coherence of the spin state due to the nuclear spin bath is likely.

The physical properties of the emitters investigated in this chapter, along with the favourable properties of the host crystal, present an exciting platform for on-chip integrated photonics. The Pockels effect can be exploited to change the birefringence of the crystal using an electric field, a key require-
ment for amplitude/phase modulation based integrated photonics. In addition, it has been shown that AlN presents a low-loss integrated platform for both visible and near-infrared photonics \[160, 161\], where AlN can be sputtered on silicon with high crystalline quality. The addition of a room temperature single photon emitter into an integrated circuit presents a pathway to off-the-shelf quantum technologies.
Chapter 4

III-Nitride Photonic Nanostructures

4.1 Introduction

One of the most fundamental requirements for any solid-state photonic technology is to maximise the amount of light directed from the source to the measurement apparatus, whether that is the human eye or a sensitive photodiode. This is especially true for quantum photonic technologies, where quantum light sources are inherently dim due to the finite spontaneous emission lifetimes of the single emitters, and any loss deteriorates the non-classical characteristics of the source. In this chapter, a number of photonic nanostructures are investigated using a finite-difference time-domain (FDTD) simulation approach as potential candidates for enhancing the light collection by external optics from single emitters in semiconductor host environments. In this chapter, all simulations were conducted using Analysis Lumerical. We start by introducing the FDTD approach and simulation environments with special considerations paid to simulation resources and computational time. A number of devices are considered, including: a solid immersion lens (SIL), a micro-pillar and a micro-pyramid. The collection efficiency (CE) from a dipole embedded in a homogeneous GaN/AlN slab is considered analytically and numerically. The impact of the sapphire growth substrate and buried SiO$_2$ disks in a specific GaN sample, which is introduced in more detail in the subsequent chapter, are investigated numerically. Two top-down photonic structures are also simulated, a micro-pillar and a micro-pyramid. The latter is proposed to take advantage of an angled reactive ion etching (RIE) technique developed in house by Gough et al. [196]. Top-down patterned structures were simulated in order to enable a deterministic lithography process as discussed in detail in Chapter 6.

4.1.1 The Finite-Difference Time-Domain Method

The FDTD simulation technique has become a popular method for investigating how electromagnetic fields interact with physical objects in the environment. By simulating in the time domain, the FDTD method facilitates broadband frequency solutions within a single simulation run. The FDTD technique
exploits a square grid-based modelling method, where the approximate solutions to time-dependent Maxwell’s equations are calculated on each node in the grid. The electric field vector components in a volume of space are solved at a given instance of time, where the magnetic field component is solved at the next instance in time. The process is repeated until the desired steady state performance is achieved. This simulates a time-dependent evolution of the electromagnetic field as it interacts with the physical environment.

To simulate a photonic structure using the FDTD method, a computational simulation region must first be specified. This domain is the physical region over which the simulation needs be performed, including any structures that may interact with the electromagnetic field. The electric field $E$ and magnetic field $H$ are calculated at each location in the simulation region, as determined by the simulation mesh. The mesh, and specifically the mesh size, dictates the accuracy of a simulation. The finer the mesh, i.e. the smaller the distance between mesh points, the more accurate the simulation becomes. However, the finer the mesh, the more computational times and memory are required to perform the computation, increasing the simulation run time. To limit the impact of the mesh size/computational time trade-off more sophisticated methods for defining the mesh have been developed. Rather than a linear mesh, where the distance between each mesh node is identical across the simulation region, one can define a mesh with a variable step size in all dimensions, facilitating a smaller step size for smaller objects and optimisation of the number of mesh nodes. Variable mesh grids can drastically improve the time and computational power required to reach the desired level of simulation accuracy.

Another technique for reducing the complexity of a simulation is to exploit symmetry around the source. The source for a generalised FDTD method may be: the current through a wire, an applied electric field and/or a plane wave. For the simulations presented in this chapter, the source is a single oscillating dipole, representing the emitters introduced in Chapter 3. Considering a dipole aligned to the X axis, see Fig. 4.1 it is intuitive to see that the dipole presents a symmetric/anti-symmetric emission pattern around the Y and X axes, respectively. This enables simulating only a quarter of the environment, reducing the simulation complexity. The simulation region must be symmetric and periodic around the dipole source to include symmetric/anti-symmetric boundary conditions.

Material properties are included in the simulation by defining the complex refractive index of the material over the collected frequency domain. In theory, any material may be included in the simulation, as long as the permeability, permittivity and conductivity are specified. In this chapter, no metallic elements are included: therefore only the complex refractive index is required. The complex refractive index for the materials investigated in this chapter are taken from the literature; GaN [197], AlN [198], sapphire [199], PMMA [200] and ZrO$_2$ [201]. It is assumed, due to the crystal properties, that the absorption coefficient $k$ is negligible for each dielectric. Therefore, all materials are modelled as homogeneous dielectric slabs.

The final consideration for the simulation environment is the monitors that measure the electric and/or
magnetic field vectors. In the simulations presented in this chapter, the monitors collect the frequency domain electromagnetic field profile across a spatial region within the total environment. Boundary conditions are defined to truncate the simulation region, where a perfectly matched layer (PML) is used to absorb the radiation at the boundary without reflection back into the simulation region. The near-field electric field profile, collected on an XY monitor close to the top surface of the environment, is used to determine the percentage of the radiation that can be collected into the first lens. An illustration of the near field profile from a simulation of a pillar is shown in Fig. 4.1 (iii). The simulation environment is illustrated in (i) and (ii). The blue and orange monitors are used to collect the near field intensity. The near-field profile is projected into the far-field, where the near-field is decomposed using a set of plane waves. The projected far field for the near field intensity in (iii) is shown in Fig. 4.1 (iv). The resultant far-field profile is integrated across the numerical aperture of the collection optics and normalised by a number of methods. Lumerical offers script commands for obtaining the power of a dipole in a simulation. The “sourcepower” (SP) command returns the power a dipole radiates in an infinite homogeneous medium. The power returned from the SP command does not represent the actual radiated power, as the real power is highly dependent on the simulation environment. Any reflections from structures in the environment interfere with the dipole field and change the radiated power. To obtain the actual radiated power, Lumerical offers the “dipolepower” (DP) command. Considering the relationship between the actual radiated power and the power the dipole would radiate in an infinite dielectric, the Purcell factor $F_p$ can be defined as,

$$F_p(f) = \frac{DP(f)}{SP(f)}.$$  \hspace{1cm} (4.1)

However, when one considers a lossy material, where the imaginary part of the refractive index (absorption coefficient) $k > 0$, the radiated power from the DP function becomes unreliable. A transmission box of monitors can be used to measure the radiated power in lossy materials. In the simulations...
in the chapter, two transmission boxes are included. The first transmission box directly surrounds
the dipole and is referred to as the “dipole box” (DPB). The second transmission box encompasses
the whole simulation region, including any physical structures, and is referred to as the “structure
transmission box” (STB). In this chapter, only dipole wavelengths between \(400 \leq \lambda \leq 1000\) nm are
considered, where the absorption coefficient is negligible with respect to the refractive index of each
material. All of the above mentioned normalisation techniques: DP, SP, STB and DPB, should yield
similar results. For the simulations where the DPB results are not presented, the box of monitors
surrounding the dipole were not included in order to avoid inflating the simulation time with a fine
mesh size around the dipole.

4.2 Single Dipole in Bulk III-Nitrides

It is well understood that extraction of light from a high refractive index material into a lens is limited
due to refraction and total internal reflection (TIR). To gain an understanding as to the losses occurred
due to refraction and quantify the enhancement for the proposed structures, a single dipole emitter
in bulk GaN is first considered. We begin the analysis by analytically determining the CE of a dipole
close to the surface of an infinite dielectric slab in order to quantify the accuracy of the FDTD method.

4.2.1 Analytical Collection Efficiency

The extraction of light from a high index material such as GaN is limited due to refraction at the high-
to-low index medium. According to Snell’s law, light escaping the high index material experiences a
change in angle of incidence \(\theta\) in the form,

\[
\frac{n_1}{n_2} = \frac{\sin(\theta_2)}{\sin(\theta_1)},
\]

where for \(n_1 > n_2\) then \(\theta_2 > \theta_1\).

The CE of a dipole in a dielectric with a finite index contrast with the immersion medium of the
optics, in this case air, can be understood considering the NA of the imaging system. The NA of the
imaging system in the dielectric is reduced due to refraction at the interface according to Snell’s law.
The NA in the dielectric is given as,

\[
\theta_{\text{GaN}} = \sin^{-1}\left(\sin(\theta_{\text{Air}}) \frac{n_{\text{Air}}}{n_{\text{GaN}}}\right) = 22.5^\circ, \quad \therefore \quad \text{NA}_{\text{GaN}} = \text{NA}_{\text{Air}} \frac{n_{\text{Air}}}{n_{\text{GaN}}} = 0.38
\]

where \(n_{\text{GaN}} = 2.35\) and \(\text{NA}_{\text{Air}} = 0.9\). Therefore, propagation angles from the dipole up to 22.5° are
collected by the imaging system. Higher angles are lost due to refraction away from the collection
half angle and total internal reflection (TIR). If one considers a index matched immersion medium, all
solid angles are able to escape the dielectric with no refraction at the interface, filling the collection
optics.

To quantify the enhancement due to the proposed photonic structures we start by determine the CE of a single dipole in an infinite dielectric slab. One can use an analytical approximation by assuming a dipole emitter close to the interface, far enough away to neglect interference effects, with a radiation pattern as measured from the in-plane X axis as [187],

$$I(\theta, \phi) = \frac{3}{8\pi} \left(1 - \sin^2(\theta) \cos^2(\phi)\right),$$  \hspace{1cm} (4.4)

where $\theta$ is the out-of-plane emission angle and $\phi$ is the in-plane azimuthal angle measured from the X axis. The intensity has been normalised so that integration over all the solid angles equals unity.

One can then determine the CE by assuming an in-plane dipole ($\phi = 0$), integrating the solid angles over the numerical aperture of the collection optics in the following form [187],

$$\eta = \frac{3}{8\pi} \int_0^{\pi/2} \int_0^{\pi} \left[1 - \sin^2(\theta) \cos^2(\phi)\right] \sin(\theta) d\theta d\phi \times T_a,$$  \hspace{1cm} (4.5)

$$\eta = \frac{1}{32} \left[15 \left(1 - \sqrt{1 - \sin^2(\theta)}\right) + (1 - \cos(3\theta))\right] \times T_a.$$ \hspace{1cm} (4.6)

Therefore, for an imaging system with NA = 0.9,

$$\theta = \sin^{-1}(\text{NA}_{\text{GaN}}) \quad \text{and} \quad T_a = \frac{4n_{\text{Air}}n_{\text{GaN}}}{(n_{\text{Air}} + n_{\text{GaN}})^2} \Rightarrow \eta_{\text{bulk}} \approx 4.6\%.$$  \hspace{1cm} (4.7)

$T_a$ is an approximation of the transmission through the semiconductor-to-air interface using Fresnel’s equations. Both the polarisation and angle of incidence are ignored by assuming normal incidence.

Assuming normal incidence, where there is no distinction between S and P polarisation, presents an overestimate for the transmission value for all solid angles, as the reflectivity for photons that approach the critical angle of TIR tends towards unity. The approximate transmission value therefore presents an upper bound for the CE from an emitter embedded in a GaN slab.

### 4.2.2 Numerical Collection Efficiency

To numerically quantify the CE for the photonic structures proposed within this chapter, a simulation of a dipole source located within a 5 µm GaN film on a sapphire substrate is presented in Fig.4.2. The dipole wavelength is set to 820 nm and a numerical aperture of 0.9 is considered. As well as the GaN film case (Fig.4.2(i-iii)) the impact of an embedded silicon dioxide (SiO$_2$) disk with a radius of 2.5 µm and a thickness of 0.5 µm is also investigated (Fig.4.2(iv,v)). The SiO$_2$ disks were investigated in order to quantify the collection efficiency for a specific sample introduced in more detail in Chapter 5. TIR is evident when comparing the electric field intensity plots (i) and (iv).
There is an oscillatory dependence on the depth of the emitter to the percentage of the light collected into the first lens in (ii). An oscillatory response is expected, due to the change in interference from reflections from the GaN-to-air interface (and the GaN-to-sapphire interface). The oscillation has a periodicity of $\lambda/2n = 190\,\text{nm}$, with the dipole wavelength $\lambda = 820\,\text{nm}$. The suppression of the oscillation around depths $0.5 - 1\,\mu\text{m}$ may arise due to the interference between the GaN-to-air and sapphire-to-air destructively cancelling out. In addition to the oscillatory behaviour, the CE agrees well with the analytical method presented in Fig.4.7 where the mean CE $4.6\%$, as illustrated in Fig.4.2(ii) with the dashed orange line, is comparable to the previously determined upper bound of 4.6%.

Fig.4.2(iii) demonstrates a convergence test simulated to determine the correct monitor size to capture the whole near field profile in the XY plane without truncating the field. A convergence to a steady state level when the monitor size is $>25\,\mu\text{m}$ is observed. The CE as a function of the Z monitor span, i.e. how far away from the GaN-to-air interface the XY monitor is located, is less dependent on the distance, as long as the monitor is placed $>\lambda/2$ away from the interface. The Z divergence test is not shown in the figure. This ensures that the evanescent field at the material interface is not projected into the far field. Determining correct monitor sizes is essential to accurately determine the CE using the far-field projection technique. Truncating the field profile leads to a sudden transient at the monitor boundary, as the far field projection algorithm assumes zero field outside the monitor. During the projection, as a Fourier transform is used, this transient materialises as a high-frequency ripple. Ensuring the field profile has decayed at the monitor edge requires large monitors for simulations such as a dipole in a semiconductor slab, increasing computational requirements. In the simulations in (i) and (iv) this problem is mitigated due to the TIR in the semiconductor, allowing the CE profile to converge.

In addition to the planar GaN case, the impact of a SiO$_2$ disk embedded in the GaN layer was investigated. Due to the orientation of the embedded disk, the anti-symmetric boundary conditions were removed. At $\text{NA} = 0.9$, the incorporation of the disk leads to a $<1\%$ increase in the CE.

The impact of the out-of-plane angle $\phi$ was considered in (vi). As one rotates the out-of-plane angle of the dipole source, the symmetry orthogonal to the dipole is lost. Therefore the anti-symmetric boundary condition was also removed for this simulation. The CE reduces with the out-of-plane angle, following the expected sinusoidal function, where the out-of-plane orientation ($\phi = 90^\circ$) reduces the CE to $<0.4\%$. This represents an order of magnitude reduction in the CE. The analysis presents an understanding into why in-plane emitters are commonly observed in III-Nitrides [176], [178], [179]. In-plane emitters are preferentially investigated due to their inherent brightness. The low CE for an out-of-plane emitter generally makes imaging and measuring their properties more challenging. To this end, out-of-plane emission is investigated for the proposed structures to quantify their ability at directing the dipole radiation towards the optics.
In conclusion, the collection of light from a high-index material results in a small percentage of the light reaching the imaging optics due to refraction at the high-to-low index interface. For an imaging system with $\text{NA} = 0.9$, $\text{CE} = 4.6\%$ and $0.4\%$ for an in-plane and out-of-plane dipole, respectively. In order to enhance the light collection into the first lens, a number of photonic structures are investigated, which act to guide photon emission towards the first lens.

### 4.3 The Hemispherical Solid Immersion Lens

The solid immersion lens (SIL), as discussed in detail in Chapter 5, exploits one of two aplanatic points imaging through a ball lens. In this subsection, the CE enhancement of an ideal hemispherical SIL is considered both analytically and numerically. A number of assumptions are made. The SIL is a perfect homogeneous hemisphere of ZrO$_2$ ($n_{\text{ZrO}_2} = 2.14$) with a flat bottom interface and no air gap between the SIL and the semiconductor. The SIL acts as an intermediate closely index matched medium, where the geometry avoids refraction at the high-to-low index interface (SIL-to-air) due to the propagation angle at normal incidence.

One can again understand the CE enhancement by considering the imaging of a dipole through a SIL. The lack of refraction increases the NA of the imaging system in the semiconductor, with
NA\textsubscript{GaN} = NA\textsubscript{Air}n\textsubscript{SIL}/n\textsubscript{GaN} = 0.81. Angles up to 54° in the semiconductor are therefore collected by the imaging system with the SIL, which represents a two fold increase in the acceptance half angle. To quantify the enhancement in CE for a dipole embedded in GaN one can use Eq.4.6 under a simplification - the SIL is assumed to be an infinite homogeneous dielectric layer where the SIL-to-air interface is considered with Fresnel equations,

\[ T_n = \frac{16n\textsubscript{GaN}n\textsubscript{SIL}n\textsubscript{Air}}{(n\textsubscript{GaN} + n\textsubscript{SIL})^2(n\textsubscript{SIL} + n\textsubscript{Air})} = 86.8\% \quad (4.8) \]

Due to normal incidence, S and P polarised effects are irrelevant, which is valid for an emitter embedded exactly at the middle of the hemisphere’s bottom surface. Using Eq.4.6 and Eq.4.8 with \( \theta = \sin^{-1}\left(\frac{n\textsubscript{SIL}NA}{n\textsubscript{Air}n\textsubscript{GaN}}\right) \) the CE with the SIL is given as \( \eta\textsubscript{SIL} \approx 22.5\% \). This represents a total CE enhancement as compared to an emitter in bulk of \( \times 4.8 \).

FDTD simulations can be used to confirm the analytically determined CE. To avoid the large computational requirements to simulate over the SIL (the SIL used in Chapter 5 is a 1 mm diameter hemisphere) a similar simplification to the analytical approach can be made. The SIL is modelled as an infinite homogeneous dielectric where the electric field monitors used to project the near-field emission pattern into the far field are embedded in the dielectric layer. Reflections are avoided by ensuring the SIL material spans the whole simulation region. The SIL-to-air interface is considered by assuming normal incidence using Fresnel’s equations. The results from the FDTD analysis of an ideal h-SIL is shown in Fig.4.3.

The analytically determined CE as a function of the imaging numerical aperture for a SIL on GaN in presented in Fig.4.3(ii). The figure illustrates the enhancement in the light collection across all imaging acceptance half angles as the plot with the SIL approaches that of a dipole imaged in free space, represented as the dotted line in the plot. Concentrating on the expected CE for an imaging system with NA = 0.9 allows direct comparison to the previously determined CE enhancement in GaN.

Due to the reduced index contrast between the SIL and the semiconductor, the CE with and without the SIL is given as \( \eta\textsubscript{SIL} \approx 22.5\% \) and \( \eta\textsubscript{AlN} \approx 4.6\% \), a \( \times 4.9 \) fold improvement. Cross-sections of the electric field intensity profile are presented in (iii) and (iv). The trapping of light in the semiconductor due to TIR is observed without the SIL (iii), while the majority of the emission with the SIL (iv) is able to escape into the first lens.

An advantage of using a solid immersion lens as a collection enhancement scheme is that the use of a dielectric to help guide light towards to the optics is inherently a broadband enhancement scheme, limited by the dispersion of the SIL and the absorption of the dielectric. Broadband collection enhancement is beneficial for the broad emission spectra observed in AlN emitters presented in Chapter 3. The analytically and numerically determined CE as a function of the dipole wavelength is illustrated in Fig.4.3(v). The analytical data illustrates the broadband enhancement, with a flat wavelength re-
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Figure 4.3: Analytically and numerically determined CE from a hemispherical solid immersion lens on AlN. i) Illustration of the cross-section in XZ of a hemispherical SIL on a 1 µm thick AlN dielectric layer. ii) Analytically determined CE with (green - filled) and without (blue - filled) a SIL, as compared to the ideal case of imaging a dipole in air (grey - dashed). iii-iv) Electric field intensity cross-section along X and Z with (iv) and without (iii) a SIL. v) CE as a function of the wavelength of the source determined analytically (symbols) and numerically (lines) with (green) and without (blue) a SIL.

The FDTD measurement is more interesting. For the case without the SIL, the calculated CE agrees well with the analytical result. An oscillation around the analytically determined value is observed. The oscillation materialises due to the wavelength dependence of the interference from the top and bottom interfaces. With the SIL, the simulated CE as a function of the wavelength diverges from the analytically determined result, due to the reflection from the AlN-to-sapphire interface, increasing the amount of light that reaches the collection optics.

4.4 Top-Down Etched Structures

4.4.1 Micro-Pillar

An effective method for enhancing the photon collection from a dipole in a high index material is to pattern deterministic structures around the dipole that act to guide the radiation towards the collection optics. One such structure is the top-down etched micro-pillar. The micro-pillar acts as a low-quality factor resonator that guides light towards the collection optics due to the index contrast between the pillar sidewalls and the surrounding environment, often air. One can therefore use FDTD to investigate the photonic response of a semiconductor micro-pillar, where physical parameters such as the pillar dimensions based on the emitter properties can be optimised. In order to investigate the performance, the simulation environment is set up as follows. A 1 µm GaN pillar on a sapphire
Chapter 4. III-Nitride Photonic Nanostructures

Figure 4.4: CE enhancement from a semiconductor micro-pillar. i) Illustration of the micro-pillar simulation environment. ii) CE as a function of the source wavelength for a dipole embedded 0.4 µm from the surface in a 1 µm homogeneous GaN layer surrounded by sapphire and air. CE (iii), Purcell factor (iv) and CE enhancement (v) as a function of the micro-pillar radius and source wavelength. The CE enhancement in (v) is normalised using (ii).

Substrate is surrounded by electric field monitors. Convergence tests were done at the largest pillar radius (1 µm) with the longest source wavelength (1 µm) to ensure the electric field monitors are far enough away from the sidewalls and top surface to avoid collecting the evanescent standing waves at the interfaces. The simulation source is a dipole emitter at a depth of 0.4 µm from the top surface of the pillar, where the wavelength of the source is varied between 0.5 and 1 µm. The near-field profile from the top surface is again projected into the far field to quantify the CE.

A baseline measurement, simulated to account for the change in thickness of the GaN layer and different dipole depth, is presented in Fig. 4.4(ii). The CE observed is consistent with the aforementioned numerical and analytical determination of the CE for a dipole in a bulk slab, with a wavelength dependent CE centred around 4.75% for an infinite semiconductor in XY. The CE and Purcell factor as a function of the pillar radius and source wavelength is presented in (iii) and (iv) respectively. A streaking pattern is present in the images, which redshifts with increasing radius, suggesting the presence of Mie resonances. Mie scattering modes have been investigated before in silicon [203], [204] and gallium arsenide (GaAs) [205] micro pillars. The CE heatmap (iii) is normalised by DP. The highest CE is 54% for a dipole with a wavelength \( \lambda = 632 \text{ nm} \). The normalised CE, which represents...
the CE enhancement, is shown in (v). A maximum 13.8 fold enhancement in CE can be observed for a dipole with $\lambda = 725\text{ nm}$. This represents a 2.8 fold enhancement in light collection as compared to the h-SIL. To quantify the emission rate enhancement one can map the Purcell factor as defined in Eq. 4.1, where moderate Purcell factors in the order of 2.5 are observed.

One can observe that the CE and Purcell factor heatmaps in Fig. 4.4(iii) and (iv) are inverse colour images. The highest CE occurs at the lowest Purcell factor and the lowest CE occurs at the highest Purcell factor. The inverse colour maps can be understood considering that the Purcell factor is dependent on the amount of light that is trapped within the photonic structure. The confinement of the light in the structure increases the probability of light escaping out of the sidewalls and bottom interface as opposed to towards the collection optics.

### 4.4.2 Upended Pyramids

In addition to the aforementioned micro-pillar structure, an angled upside-down pyramid structure is also considered as illustrated in Fig. 4.5(i). The structure is proposed to take advantage of a top-down angled etch technique recently demonstrated in GaN by Gough et al. [196], with the proposed improved collection due to the angled facets of the pyramid acting to reflect light upwards towards the collection optics.

Figure 4.5 illustrates the CE for an angled pyramid. A similar red-shifting streaking pattern is observed in (ii) and (iii), again attributed to Mie scattering within the pyramid. The highest CE = 58.6\% at a wavelength $\lambda = 614\text{ nm}$ represents a 4.6\% improvement over the vertical wall micro-pillar. The micro-pyramid presents an up to 14.2 fold enhancement in CE compared to a dipole in bulk. One can also observe how the CE streaking pattern is more broadband as compared to the micro-pillar. Due to the improved performance of the pyramid, the structure is investigated in more detail, specifically with regards to: the dipoles’ in-plane and out-of-plane angles (iv), the number of sides of the pyramid (v) and off-centred location of the dipole (vi).

The angular dependence of the emitter is investigated in Fig. 4.5(iv). The in-plane angle ($\theta$) and out-of-plane ($\varphi$) angles are considered. There is no dependence on the in-plane angle for a dipole at the centre of the structure, which is advantageous in reducing emitter preselection requirements. However, there is a dependence on $\varphi$, which is expected when one considers the direct rotation of the dipole radiation pattern away from the collection optics. However, when the dipole is completely out-of-plane, $\varphi = 0^\circ$, where normally a very small amount of the light would reach the collection optics, a 20\% CE is still obtained. This result can be normalised by the out-of-plane CE for the bulk case, as presented in Fig. 4.2(vi). Although the CE decreases to 20\%, the enhancement of the collected light due to the pyramidal structure is greater than $\times50$. This overcomes one of the greatest difficulties with studying out-of-plane emitters, their low light extraction from high index materials. To date, it is unknown if out-of-plane emitters are present in GaN and/or AlN, as previous works concentrate
Figure 4.5: CE from a pyramidal photonic structure. i) FDTD simulation environment illustration. ii) CE as a function of the source wavelength and top radius of the pyramid. The bottom radius is set at 50 nm. iii) Purcell factor as a function of wavelength and top radius. iv) CE as a function of the dipole in-plane $\theta$ and out-of-plane $\phi$ angle. v) CE as a function of the number of sides of the pyramid, where the greater the number of side facets the more conical in shape the structure becomes. vi) CE as a function of the dipole in-plane displacement.
their attention on brighter in-plane emitters.

The dependence of the CE on the number of sides of the pyramidal structure is also investigated in Fig.4.5(v), where the wavelength $\lambda = 820\text{ nm}$. The plot illustrates the reduction in CE with respect to the number of sides, where the pyramidal structure becomes more conical with the number of sides. This reduction is attributed to a change in the scattering modes within the structure at the dipole wavelength and structure dimensions. Later in the chapter a conical structure which provides similar results as to the pyramidal structure is demonstrated. Finally, the dipole is displaced away from the centre of the pyramid structure in (vi). A reduction in the CE is observed, highlighting the importance of deterministic patterning of the pyramidal structure spatially aligned to the dipole.

4.4.3 Normalisation

The CE values presented thus far are determined by normalising the integrated far field intensity by the DP function. This represents the total amount of light collected by the first lens excluding any emission rate enhancement from the Purcell effect. If one assumes continuous wave (CW) optical excitation of the dipole, it is apparent how both the emission rate and CE enhancement would lead to a photon detection rate that would exceed the predicted value from the normalised CE value. However, one can measure independently the Purcell enhancement and CE enhancement using a pulsed excitation scheme. Consider a single emitter with antibunched photon statistics, where the photon number distribution is a delta function with mean photon number equal to one. One and only one photon would be detected after each excitation pulse. The measurement of a subsequent photon would only occur after the application of a second excitation pulse. Therefore, the number of photons detected per unit time is independent on how quickly the source emits the photons. In addition, measuring the lifetime of a emitter would enable direct comparison of the emission rate with and without the photonic structure.

4.4.4 Mie Scattering

Although enhancement of the CE was the primary aim for the structures investigated in this chapter, there is an enhancement of the Purcell factor for both the micro-pillar and micro-pyramid structures. The streaking pattern present within the CE and Purcell factor images suggests, as previously discussed, the presence of Mie scattering within the structure. In order to illustrate this process, the radius of the pillar and the top radius of the pyramid are set to 550 nm and the wavelength dependence on the Purcell factor is considered. This is illustrated in Fig.4.6(i). The left-hand-side of the image and right-hand-side of the image represent the pillar and pyramidal structure respectively. Clear peaks in the Purcell factor as a function of the wavelength can be determined, which each represent different fundamental Mie scattering modes. As the field within the structure is scattered internally, the scattered light interferes with the dipole field causing constructive and destructive interference, which
results in an enhancement and reduction of the Purcell factor, respectively. Consider a wavelength where the CE is low but the Purcell factor is high. As light is scattered within the structure, it is less likely to escape in the direction of the collection optics, which is detrimental when one is interested in the CE. Some of the features in the spectrum attributed to these modes are labelled and the electric field intensity at each labelled mode wavelength is presented in (ii). For each of the electric field plots, the electric field intensity $|E|^2$ profile illustrates the resonances within the structure.

## 4.4.5 Pyramidal Vs Conical Structure

The pyramidal structure can be transformed into a conical structure by increasing the number of side facets. This was briefly investigated in Fig 4.5 (v) with a significant reduction in the CE as a result of the greater number of sides. It was previously suggested that this could likely be due to a shift in the Mie scattering modes within the structure due to the change in geometry. The conical structure is worth investigating due to the ease of fabrication relative to the pyramidal structure. Intuitively such
a geometry could provide enhanced collection as it is less faceted and may produce a more Gaussian far field profile, which is better for coupling into a single mode fibre. Therefore, the conical structure is investigated in more detail in Fig. 4.7. The CE and Purcell factor plots as a function of the dipole wavelengths are not presented, but produced similar results as to that of the pyramidal structure albeit with different scattering modes. One slight deviation was the introduction of a single mode between 500 – 540 nm which spiked to a Purcell factor of 5. The top radius of the conical structure was between 600 and 700 nm. A 2.2% increase in the maximum CE of 60.8% was observed as compared to the pyramidal structure.

The far field emission pattern, taken by projecting the near field emission (ii,v) one meter above the structure, is demonstrated in Fig. 4.7 (iii,vi). i) and iv) shows the absolute square electric field intensity across a XZ monitor through the centre of the structures on a logarithmic colour scale. For both the pyramidal and conical structure, the dimensions are set for a high CE at the dipole wavelength of 650 nm. Directionality of the E field towards the collection optics in the +Z direction can be seen in Fig. 4.7 (i,iv). The near field intensity profiles further suggest a strong localization of the E field in the X and Y plane, which is apparent in the normalised far field projections. This produces a modal pattern of the emission, with the majority of the emission falling within the 20° polar angles, well suited for coupling into single mode fibre using low numerical aperture coupling optics.

4.5 Conclusion and Future Outlook

In conclusion, a number of photonic structures and devices were investigated analytically and numerically to quantify the CE enhancement. Top-down patterned devices were considered, along with a hemispherical solid immersion lens, in order to be compatible with a proposed deterministic patterning technique discussed in Chapter 6. An in-plane dipole in a homogeneous slab of GaN was considered, to serve as a baseline CE for comparison. A good agreement between an analytically determined and numerically determined baseline was achieved, where a wavelength and depth dependent CE centred around 4.6% is observed. A geometric enhancement scheme was considered using a hemispherical solid immersion lens. The reduced refractive index contrast between the immersion medium of the collection optics and the semiconductor mitigated refraction at the semiconductor interface. The CE is investigated both numerically and analytically, where a good agreement is also observed. The CE enhancement with the SIL is predicted to be ×4.8. This is explored in more detail in Chapter 5.

Top-down etched structures were then considered. By varying the radius of a pillar with vertical sidewalls, the CE as a function of the pillar dimensions and source wavelength was investigated. A red-shifting streaking pattern was observed in both the CE and Purcell factor images, likely due to the structure supporting Mie scattering modes in the pillar. Engineering the pillar radius for a specific emission wavelength therefore facilitates the collection of up to 13 times more light for an in-plane
Figure 4.7: Pyramidal vs conical collection efficiency. i) Electric field XZ cross-section for the highest CE for a pyramid with top radius of 500 nm with a source wavelength of 650 nm. ii) Near field electric field profile taken on the XY monitor 1 µm above the pyramid top surface. iii) Projected far field normalised electric field intensity profile calculated from the near field data in (ii). iv-vi) Corresponding electric field intensity profiles for a conical structure with a top radius of 738 nm.
### Table 4.1: Analytical and simulated CE for the structures proposed. The collection enhancement with respect to an emitter embedded within bulk GaN is also presented. Upper bounds are given for dimension dependent structures. All values do not include Purcell enhancement to the emission rate.

<table>
<thead>
<tr>
<th>Structure</th>
<th>Analytical CE (%)</th>
<th>Simulated CE (%)</th>
<th>CE Enhancement</th>
</tr>
</thead>
<tbody>
<tr>
<td>Planar (In-Plane)</td>
<td>4.6</td>
<td>4.6</td>
<td>-</td>
</tr>
<tr>
<td>Planar (Out-of-Plane)</td>
<td>-</td>
<td>0.4</td>
<td>-</td>
</tr>
<tr>
<td>Planar with SiO$_2$ Disk</td>
<td>-</td>
<td>~4.9</td>
<td>1.06</td>
</tr>
<tr>
<td>SIL (No Gap)</td>
<td>26.7</td>
<td>29.5</td>
<td>6.34</td>
</tr>
<tr>
<td>SIL (100nm PMMA)</td>
<td>-</td>
<td>21.5</td>
<td>4.64</td>
</tr>
<tr>
<td>SIL (100nm Air)</td>
<td>-</td>
<td>14.0</td>
<td>3.04</td>
</tr>
<tr>
<td>Micro Pillar</td>
<td>-</td>
<td>≤ 54</td>
<td>≤ 13.3</td>
</tr>
<tr>
<td>Micro Pyramid (In-Plane)</td>
<td>-</td>
<td>≤ 59</td>
<td>≤ 13.7</td>
</tr>
<tr>
<td>Micro Pyramid (Out-Of-Plane)</td>
<td>-</td>
<td>≤ 20.6</td>
<td>≤ 52</td>
</tr>
<tr>
<td>Micro Pyramid (Conical)</td>
<td>-</td>
<td>≤ 61</td>
<td>≤ 14.2</td>
</tr>
</tbody>
</table>

dipole, not including the enhancement in photon detection rate due to the Purcell effect enhancement. For an out-of-plane dipole, the pillar and angled pillar structures present an even more enhanced mean to guide light towards the collection optics, with a maximum CE of 54 and 61 % for the pillar and pyramidal structure respectively. A summary of the investigated devices is given in Table 4.1.
Chapter 5

Solid Immersion Lens Enhanced Microscopy of Quantum Emitters

5.1 Introduction

One of the fundamental challenges for quantum photonic technologies in the solid state is the extraction of light from high refractive index materials such as GaN and AlN. The finite refractive index contrast between the host medium and immersion medium of the optics leads to refraction and total internal reflection at the interface, reducing photon collection from the emitter. In this chapter, a geometric technique for increasing the number of photons collected from III-nitride quantum emitters is introduced. The technique exploits a solid immersion lens (SIL), a solid state lens with a refractive index close to the host material. It is shown that, due to the reduced index contrast and geometry of the lens, imaging single emitters with an in-situ SIL leads to an increased photon collection efficiency (CE) and improved imaging resolution. Two experiments explore the SIL in detail. The first exploits a deterministically placed hemispherical SIL (h-SIL) to demonstrate enhanced single emitter spectroscopy, quantifying the imaging and CE enhancement on a single pre-determined emitter with and without the SIL. A deterministic pick-and-place system is developed and introduced that facilitates few-micron accuracy of the spatial alignment of the lens to the emitter. The second experiment uses a statistical analysis over 500 sampled emitters in AlN to demonstrate a strong dependence of the CE on the thickness of the intermediate layer used to adhere the lens to the sample. Using a finite-difference time domain approach it is illustrated that the enhancement materialises due to the coupling of an evanescent field through the intermediate layer at thin film thicknesses, a phenomenon known as frustrated total internal reflection.
5.1.1 Review of the Literature

As previously determined in Chapter 4, one can exploit the geometry of a SIL, a truncated sphere of a high refractive index dielectric, to enhance the number of photons measured from an emitter in a high index material. Born and Wolf [206] determined that imaging through a sphere results in aberration free imaging at one of two aplanatic points. The two aplanatic points became the basis for the two SIL geometries, the hemispherical (half ball) and Weierstrass geometry. The SIL was first discussed in the context of microscopy by Mansfield and Kino [207]. They demonstrated, using a scanning optical microscope, that mounting a hemispherical SIL to the surface of a sample reduces the optical resolution by the inverse of the index of the SIL. However, it was not until the work by Koyama et al. [208] that a SIL was used in the context of increasing the CE of a fluorescent emitter. In this pioneering work, fluorescent polystyrene beads are distributed on the bottom surface of the SIL using an evaporated water-bead solution. They quantify the enhancement by measuring the fluorescence from the beads through the SIL and comparing the intensity to a baseline measurement with the SIL flipped upside-down, imaging the beads without the SIL. After paying careful consideration to the specific imaging technique used they present an enhancement factor of 4.7 with the SIL.

It was not long until SILs were used to image quantum emitters [187], [209], [210], where Barnes et al. [187] developed an analytical expression for determining the CE of an in-plane dipole with and without the SIL. Ippolito et al. [211] developed a theoretical analysis for sub-surface imaging of objects, an analysis that quantifies the aberrations introduced when imaging away from the centre of the SIL. In this analysis, they show that the lateral and axial volume of the PSF when imaging through a hemispherical SIL is decreased by a factor of the index squared and cubed respectively. In addition, they theorise the impact on sub-surface imaging of an object with an air gap between the SIL and sample. They state that an air gap an order of magnitude smaller than the wavelength of the light leads to an order of magnitude reduction in the CE and a Strehl ratio below 0.1. The Strehl ratio quantifies the quality of an optical image by comparing the intensity of the image from a point source to that of an aberration free image. Vamivakas et al. [212] demonstrated a strong increase in the coupling of light to a solid state quantum emitter thanks to the geometry of the SIL, an interesting prospect for photon-matter interactions for future quantum technologies.

The aforementioned experiments into SIL-assisted microscopy focused on adhering millimetre scale SILs to samples of interest using mechanical clamping techniques to avoid formation of an air gap. Whilst able to demonstrate a significant imaging enhancement, these works were limited due to aberrations and optical losses from the material interfaces. Hadden et al. [213] proposed directly etching SILs into diamond in order to avoid the aberrations. Micro-scale SILs were etched into polycrystalline diamond using a focused ion beam (FIB) milling technique. Using a finite difference time domain approach they predict an enhancement factor of 5 for their scheme. Experimentally, a enhancement of up to 10 times is observed, dependent on the NV centers’ displacement from the centre of the SIL.
The authors attribute the greater than expected enhancement to the reduced aberrations imaging with the SIL as opposed to imaging through the planar diamond. Whilst this initial demonstration was inherently stochastic and relied on fabricating SILs with a low probability of containing an emitter at the centre of the SIL, the authors followed this initial demonstration with a more deterministic fabrication process involving markers on the sample surface \[214\]. Incorporation of fabricated SILs in diamond facilitated some impressive demonstrations of quantum photonic technologies, including the demonstration of a spin quantum register \[215\] and quantum error correction \[216\].

5.2 The Hemispherical Solid Immersion Lens

5.2.1 Motivation and Geometry

The first of the two aplanatic points formed imaging through a high index sphere occurs at the sphere centre. This aplanatic point therefore forms the basis of the hemispherical SIL (h-SIL). After dissecting the sphere along its centre, one can image through the SIL with no aberrations as each incoming ray is at normal incidence to the semicircular surface of the SIL. Conversely, each ray escaping the SIL is normal to the surface. Assuming an index match between the SIL and semiconductor, the SIL eliminates refraction. It is the reduced refraction of light entering and leaving the SIL that leads to an enhancement in the imaging resolution and CE. An illustration of the enhancement in imaging and light collection from a high-index dielectric is presented in Fig. 5.1. A ray tracing program, written in Matlab, allows one to trace the refraction of light leaving and entering the semiconductor with and without the SIL respectively. In the plots, the SIL is not perfectly hemispherical in order to demonstrate imaging and collection from a sub-surface point. The enhancement in CE is illustrated in Fig. 5.1(iii-iv). An emitter is modelled with a series of rays over a ±60° range. Without the SIL, light is trapped in the semiconductor, in this case GaN with a refractive index \(n_{\text{GaN}} = 2.35\) (at 815 nm), due to total internal reflection (TIR). The enhancement in CE with the SIL is apparent in (iv) where a h-SIL is included in the ray tracing. The SIL is modelled as a ZrO\(_2\) dielectric with refractive index \(n_{\text{SIL}} = 2.13\) (at 815 nm). Every ray is able to escape the semiconductor with minimal refraction at the semiconductor-to-SIL interfaces, due to the small index mismatch between the semiconductor and SIL.

5.2.2 Magnification and Imaging Enhancement

The aforementioned enhancement in imaging resolution can also be understood in the ray tracing simulations in Fig. 5.1(v-x). The rays originate from an imaging system with an \(\text{NA} = 0.75\) and not an emitter in the semiconductor. The plots (v) and (vi) illustrates the rays when the imaging system is on axis with the SIL focused to a point below the semiconductor surface. The effect of displacing the imaging system in the lateral (vii,viii) and axial (ix,x) direction is illustrated in the figure. Comparing
Chapter 5. Solid Immersion Lens Enhanced Microscopy of Quantum Emitters

Figure 5.1: The solid immersion lens. i-ii) Illustration of the two aplanatic points imaging through a ball lens, which illustrates the basis of the hemispherical (i) and Weierstrass (ii) SIL. iii-iv) Ray tracing of a isotropic emitter in GaN without and with a hemispherical SIL respectively, illustrating the enhanced CE using a hemispherical SIL. v-x) Ray tracing demonstrating the SIL enhanced imaging for objects embedded in a high-refractive index material. The increased NA (v,vi), reduced displacement in X (vii,viii) and reduced displacement in Z (ix,x) are illustrated without (left, blue lines) and with (right, green lines) a hemispherical SIL.
plots (vi), (viii) and (x) with plots (v), (vii) and (ix) one can conclude that: i) the effective NA in the semiconductor is close to the NA of the imaging system, ii) any displacement of the imaging optics along the X, Y or Z axis away from the SIL centre results in a lensing effect, which illustrated the increased magnification of the imaging system. The magnification can be understood by considering the ‘optical lever’ effect of the SIL, where the relationship between the displacement due to a change in X, Y or Z with the SIL ($\delta x_{SIL}, \delta y_{SIL}$ and $\delta z_{SIL}$) and without the SIL ($\delta x, \delta y$ and $\delta z$) is:

$$\delta x_{SIL} = \frac{\delta x}{n_{SIL}}, \quad \delta y_{SIL} = \frac{\delta y}{n_{SIL}} \quad \text{and} \quad \delta z_{SIL} = \frac{\delta z}{n_{SIL}^2} \quad (5.1)$$

An illustration of the change in displacement in X with and without the SIL is given in Fig. 5.2. One can observe that an imaging system displaced by $\delta x = 300 \mu m$ is displaced with the SIL by $\delta x_{SIL} = 128 \mu m$ in accordance with Eq. 5.1. One can observe a change in focal depth as the imaging system is displaced away from the centre point. It is also apparent that the imaging is aberrated away from the centre point. The larger the SIL, the further one can displace the imaging system in X and Y without introducing aberrations. This justifies the use of millimetre scale SILs as opposed to smaller micro-machined SILs [213], reducing the requirements for accurate spatial alignment.

The focal depth with and without the SIL as the imaging system is displaced in the axial direction is shown in Fig. 5.3. The dashed lines in the plot represent the imaging NA without refraction. Without the SIL, the refraction at the interface and the reduction of the NA in the semiconductor is apparent. Refraction at the planar air-to-semiconductor interface results in an increased rate of change of focus in the semiconductor. Consider the expected focus at $Z_{exp} = -100 \mu m$. The focal depth located at $100 \mu m$ illustrates sub-surface imaging without and with a SIL. Aplanatic imaging therefore occurs at a focal depth of $0 \mu m$. Without the SIL, refraction leads to an aberrated focus $Z_{GaN} = -235 \mu m$. The actual depth of focus is increased by a factor of the index of the semiconductor. Including the SIL in the ray tracing reduces the depth of focus to $Z_{SIL} = -50 \mu m$. This reduced focal depth can be understood considering the sub-surface imaging and the index of the SIL. Sub-surface imaging with a hemispherical SIL results in rays at a finite angle away from normal incidence. The refraction acts to change the depth of focus where the change in depth is related to the index of the SIL. This effect, coupled with the lack of refraction at the semiconductor interface, materialises as a change of imaging depth, $Z_{GaN}/Z_{SIL}$, that is related to the square of the index of the SIL. This is quantified in the ray tracing where $Z_{GaN}/Z_{SIL} = 4.7 \approx n_{SIL}^2$. The insets in Fig. 5.3 illustrate the reduced aberrations imaging through a SIL with a finite index mismatch.

In addition to the increased magnification when imaging through a hemispherical SIL, the lack of refraction maps the full NA into the semiconductor. This enhances the resolving power and resolution of the imaging system. One can quantify the enhancement in imaging resolution by considering the spot size of a focused Gaussian beam. One method to define the spot size $\Theta_{FWHM}$ is to use the
Figure 5.2: Ray tracing simulation illustrating the change in displacement in X when imaging without (top) and with (bottom) a hemispherical SIL.
Figure 5.3: Ray tracing simulation using incident beams focused 100 µm in the semiconductor covering an NA of 0.75. Change in displacement in Z when imaging without (top) and with (top) a hemispherical SIL. The dashed line represents the rays if no refraction occurred in the imaging. The insets illustrate the reduced aberrations when imaging through the hemispherical SIL.
Rayleigh criterion, as introduced in Eq. 2.2. For an aberration free confocal microscope,

$$\Theta_{\text{FWHM}} = 0.51 \frac{\lambda}{NA}.$$  \hfill (5.2)

The increase in resolution can be understood considering the following. Imaging through a dielectric reduces the NA and the wavelength $\lambda$ by the refractive index. Ignoring spherical aberrations, $\Theta_{\text{FWHM}}$ is the same in air and a dielectric. Including an index matched SIL scales the NA in the semiconductor by the index of the SIL. As $\Theta_{\text{FWHM}} \propto 1/\text{NA}$, the spot size is reduced by the index of the SIL.

### 5.2.3 Transfer System

The system developed to deterministically align a hemispherical SIL to an emitter is illustrated in Fig. 5.4. A micro-manipulation process was designed where a layer of a semi-adhesive polymer, in this case polydimethylsiloxane (PDMS), is used to pick and place the SIL using a glass slide attached to a motorized XYZ stage. Imaging of the SIL is achieved using an off-the-shelf wide-field microscope from Nikon with a number of different magnification microscope objectives. Due to the inherent transparency of the glass slide, the PDMS and the SIL, one can image through the SIL for coarse spatial alignment. Metallic markers are patterned and deposited on the surface of the samples using a lift-off based lithography process. The transfer process is illustrated in the following.

A SIL is picked up using the PDMS layer, as illustrated in Fig. 5.4(i). Imaging through the glass slide and PDMS one can determine when the PDMS and SIL are in contact. A small deformation of the PDMS distorts the image of the top surface of the SIL. A polymer spacer is applied to the semiconductor to avoid forming an air gap. The sample is then heated to allow thermal re-flow of the spacer used, in this example Poly(methyl methacrylate) (PMMA). PMMA is heated above its glass transition temperature ($t_g = 105^\circ$), causing a phase change of the PMMA into its liquid phase. Once heated, the PMMA is able to fill any surface imperfections in the SIL and sample surface. The SILs are polished by hand on diamond polishing sheets to reduce surface imperfections. An unpolished and polished SIL is shown in Fig. 5.5(iii). The SIL is displaced over the sample to the approximate...
location of the emitter using a three-axis motorised stage. After spatial alignment to the emitter location, the SIL is carefully placed on the surface. Contact is apparent due to a change in the film thickness of the PMMA, resulting in a colour change of the film. Upon contact, the SIL is held in place for a time to allow the PMMA to fill in any surface imperfections. The sample is then cooled to below the glass transition temperature, re-hardening the polymer and adhering the SIL to the surface. Constant pressure is applied during cooling to avoid displacement of the SIL due to thermal expansion/contraction. Once cooled, the glass slide can be displaced in Z to disconnect the SIL from the PDMS. The transfer system is used in both experiments presented in this chapter, where the first measurement uses an off-the-shelf mounting medium (Cargille Meltmount) which melts at 70°C and has a high refractive index across the visible spectrum equal to 1.7. Due to the solid state of the Meltmount at room temperature, the Meltmount was applied to the semiconductor by hand. Thin layers are achieved by mechanically pushing the SIL into the semiconductor using the glass slide. Accurate control of the film thickness was not possible. To investigate the impact of varying spacer thickness for the second experiment in this chapter, PMMA was used as a spacer medium which has a lower refractive index of $n_{PMMA} = 1.5$.

An illustration of the accuracy of the transfer process is shown in Fig.5.5(ii). The pre-determined emitter location is labelled using a red dot. The metallic crosses patterned on the sample surface can been seen in the images. Direct comparison between the crosses under and off the SIL illustrates the
magnification of the imaging system through the SIL. The distortion of the imaging system away from the centre of the SIL can also be observed in the image. The intensity of the reflection can be used to determine the centre of the SIL.

5.3 Deterministically Enhanced Imaging of a Single Emitter

In this experiment, the deterministic enhancement of the imaging resolution and light CE of a single emitter is demonstrated. A semi-polar GaN sample was chosen which demonstrated room temperature single photon statistics from a near-infrared emitter. Initially, the sample is introduced and the optical properties of the emitter are discussed in detail. The imaging enhancement and CE enhancement are subsequently considered analytically and experimentally.

5.3.1 Gallium Nitride Quantum Emitter

The sample selected for this experiment is a semi-polar GaN sample from Seren photonics. A description of the sample can be found in the appendix. SiO$_2$ disks are visible in the confocal scan map in Fig.5.6(ii). Localised emission is observed at the centre of the scan map in (ii) corresponding to the emitter of interest. A spectral measurement of the emission from the emitter is shown in (i). The spectrum is fit using two Voigt functions representing the ZPL and a red-shifted PSB. The ZPL is centred around 815 nm. The FWHM of the ZPL is $5.75 \pm 0.03$ nm. The overall spectrum is narrower than that observed from the NV$^-$ centre in diamond and AlN, in which the PSB dominates the spectrum with a room temperature broadening greater than 100 nm. The ZPL contains 39% of the total intensity as compared to <4% for diamond and AlN. A polarisation measurement reveals the out-of-plane single dipole like emission from the colour centre. The shape of the polarisation measurements is assumed to be a result of a finite azimuthal angle $\phi$. A fit to the data, using Eq.3.1, reveals an out-of-plane angle $\phi = 29.2 \pm 0.7^\circ$. For quantifying the CE enhancement, it is hypothesised that the application of the SIL will present a greater CE enhancement for a dipole with a finite azimuthal angle. Assuming the low polarisation extinction ratio is due to an out-of-plane component presents an upper bound for the CE enhancement seen in the measurements. The azimuthal angle has no impact on the lateral resolution.

5.3.2 SIL Enhanced Imaging

Using the aforementioned transfer system, a 1 mm diameter ZrO$_2$h-SIL was deterministically placed on the GaN sample spatially aligned to the emitter shown in Fig.5.6(ii). The SIL was adhered to the sample using a mounting medium, Cargille Meltmount. The Meltmount medium was chosen due to the high refractive index of $n_m = 1.7$ and the ability to melt the medium for application of the SIL, as previously discussed. The finite index contrast between the semiconductor and mounting medium
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Figure 5.6: Optical properties of the GaN emitter. i) Spectral measurement of the fluorescence from the emitter, showing a strong ZPL centred at 815 nm. ii) Confocal scan map of the Seren sample, where the SEREN1 emitter is highlighted in the image. iii) Polarisation-resolved optical measurements of the absorption dipole on the emitter, revealing a dipole radiation pattern.

Figure 5.7: Enhanced imaging of a colour centre with a SIL. i) and iv) Confocal scan maps around the defect without and with a SIL, respectively. The dashed blue lines illustrate the embedded SiO2 disks. ii) and iii) X and Y cross sections of the scan map in i). v) and vi) Confocal cross sections in X and Y for the scan map of the same defect with the SIL. All cross sections are fitted with Gaussian functions.
results in TIR at the interface. The critical angle of TIR $\theta_c$ is directly related to the index contrast in the following form,

$$\theta_c = \sin^{-1}\left(\frac{n_m}{n_{GaN}}\right) = 46.3^\circ.$$  \hspace{1cm} (5.3)

To match the critical angle for TIR, a NA = 0.75 microscope objective lens was chosen which correlates to an acceptance half angle of $\theta = \sin^{-1}(NA) = 48.5^\circ$. This enabled quantifying the enhancement in CE with the SIL, without losses due to TIR at the semiconductor-to-polymer interface.

Imaging of the emitter was achieved using the confocal microscope presented in Chapter 2. The same emitter was identified using metallic markers on the sample surface, as shown in Fig. 5.5(ii). Spectral measurements were used to ensure the same emitter was addressed by comparing the ZPL wavelength. The outline of the SiO$_2$ disks are apparent in the scan maps in Fig. 5.7. The optical spot was translated across the same angular range in both scans, corresponding to a $10 \times 10 \mu m$ displacement without the SIL. A magnification of the image can be seen with the SIL. The axis of the image with the SIL was scaled in accordance with Eq.5.1 to account for the magnification. A dashed circle with a diameter of $5 \mu m$ is overlaid on the image and positioned on top of the disk. It is apparent from the overlay that the scaling is appropriate.

Comparing the scan maps (i) and (iv) in Fig. 5.7 one can observe that the emitter has the same angular size. This can be understood considering that the increased magnification is negated by the improved optical resolution. Line scans across the emitter quantify the enhancement in lateral resolution due to the SIL. X and Y slices across the emitter were fitted using a Gaussian function. The comparison of the FWHM as determined from the fits as compared to the Rayleigh criterion, as introduced in Eq.2.2, is presented in Tab. 5.3.2. The uneven sample/SIL surface and chromatic behaviour of the objective prevented the imaging system reaching the resolution limit. Nevertheless, the data reveals an enhancement in resolution with the SIL. A measurement with a NA = 0.9 objective is included in the table. As opposed to the measurement in Fig. 5.7, the resolution with the higher NA reaches the Rayleigh resolution. This is accredited to the enhanced chromatic behaviour of the lens. With the SIL, the lateral resolution is close to the Rayleigh limit, with the best resolution of $230 \pm 5 \text{ nm}$. The discrepancy between the measured and theoretical resolution with the SIL for the measurements with the NA = 0.9 objective is again accredited to surface imperfections.

The SIL enhanced imaging in the axial direction is illustrated by measuring the Raman spectrum as

<table>
<thead>
<tr>
<th></th>
<th>NA=0.75</th>
<th></th>
<th>NA=0.9</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>X (nm)</td>
<td>Y (nm)</td>
<td>Rayleigh Criterion</td>
<td>X (nm)</td>
</tr>
<tr>
<td>No SIL</td>
<td>693±9</td>
<td>755±9</td>
<td>544</td>
<td>440±20</td>
</tr>
<tr>
<td>With SIL</td>
<td>416±6</td>
<td>417±6</td>
<td>255</td>
<td>247±4</td>
</tr>
</tbody>
</table>

Table 5.1: Lateral FWHM imaging resolution of the GaN emitter with and without the SIL as compared to the Rayleigh criterion.
Chapter 5. Solid Immersion Lens Enhanced Microscopy of Quantum Emitters

Figure 5.8: Stoke-shifted Raman microscopy based depth profiling. i) Stoke shifted Raman spectra of the Seren sample with labelled GaN phonon modes. ii) Raman spectra as a function of the focal depth of the imaging system without the SIL. iii) A slice of the depth-dependent spectra in (ii) by binning the spectral intensity around the $E_2$ high phonon line. iv) Corresponding Raman spectra as a function of depth with the SIL. The $E_2$ high binned slice with the SIL is shown in (v).

a function of the depth. The Raman measurement is taken by varying the focal depth of the imaging system and measuring the Raman signature of the epilayer as a function of depth. The Stokes-shifted Raman spectra were taken using a sharp linewidth frequency doubled Nd:YAG excitation laser and high-performance spectral filters. The imaging was displaced into the semiconductor using a piezo-actuated sample stage. The Raman spectrum of the Seren sample is shown in Fig.5.8(i). Various phonon modes can be identified from the literature [185], [197]. The depth resolved Raman measurement taken without the SIL is shown in (ii). A depth dependence on the Raman intensity is observed. Binning each spectrum around the E$_{2}$(high) phonon mode enabled fitting a Gaussian to the depth resolved intensity. The binned intensity is shown in (ii). A Gaussian fit to the depth resolved data without the SIL reveals a FWHM = 2.36 ± 0.05 µm. The same measurement with the SIL is shown in (iv). The E$_{2}$(high) phonon mode is again binned to reveal a FWHM = 10.4 ± 0.3 µm. Comparing the FWHM values with and without the SIL, one can see that FWHM is 4.4 ± 0.2 times larger with the SIL, where $\sqrt{4.4 ± 0.2} = 2.10 ± 0.05 ≈ n_{\text{SIL}}$. The FWHM with the SIL has increased by a factor of the refractive index of the SIL squared in accordance with Eq.5.1. No improvement in the imaging resolution in the axial direction is demonstrated here due to the large size of the object being imaged. Imaging an emitter, a point source, enables quantifying the enhanced resolution. Analogous to the enhancement in imaging in X and Y, the apparent size of the emitter in the axial direction would appear the same in an unscaled depth resolved measurement. The reduced Rayleigh length is negated by the axial magnification. A fluorescence line scan as a function of the focal depth with and without the SIL presents a FWHM of 3.64 ± 0.02 µm and 3.02 ± 0.04 µm, respectively. This represents an axial resolution with the SIL with a FWHM = 3.64 ± 0.02/$n_{\text{SIL}}^2 = 0.802 ± 0.004$ µm. Fluorescent line-scans across other emitters demonstrated FWHMs without the SIL closer to 1 µm. This results in a projected SIL enhanced axial resolution of 0.22 µm.

5.3.3 SIL Enhanced Collection Efficiency

To investigate the enhancement in CE, power-dependent photon counting measurements were taken with and without the SIL. The collected fluorescence was coupled into SMF28 with a MFD(1550 nm) = 10 µm. At the ZPL wavelength of the emitter, modes beyond the fundamental mode are supported in the fibre. Under-filling the collection fibre impacts the imaging resolution but ensures that all solid angles from the objective are coupled into the SMF to maximise coupling efficiency.

To maximise absorption the excitation polarisation was aligned to the dipole. No polarisation optics were included in the collection path of the microscope. It was previously suggested that the CE enhancement for a finite azimuthal angle would present a greater CE enhancement as opposed to the ×4.8 for an in-plane dipole. FDTD simulations were used to determine the azimuthal angle dependence of the CE. The simulation environment was set up as described in Chapter 4.1.1. The anti-symmetric boundary condition orthogonal to the dipole moment was removed from the simulation...
as the symmetry is lost when the dipole is rotated in the azimuthal plane. The CE enhancement as a function of the azimuthal angle is presented in Fig.5.9(i). The CE follows the expected sinusoidal dependence on the azimuthal angle with and without the SIL, as expressed in Eq.3.1. Conversely, the CE enhancement increases as the azimuthal angle increases. At $\phi = 29^\circ$, the simulated CE enhancement is $\times 5.2$ with a collection efficiency of 2.5 and 13.2% without and with the SIL, respectively. The Meltmount adhesion layer used in the experiment was not included in the simulation, as the layer thickness is unknown and difficult to measure directly below the SIL. This simulated enhancement therefore represents an upper bound of the enhancement for a dipole with an azimuthal angle $\phi = 29^\circ$.

The measured CE enhancement is shown in the power-dependent photon counting measurement in Fig.5.9(ii). The image of the SiO$_2$ disks in the scan maps in Fig.5.6(ii) and Fig.5.7 presents a background signal that is removed from the data by measuring the power dependence of a location on the disk. The background fluorescence is attributed to a Raman signature from the SiO$_2$ and/or scattering of the laser on the disk. The enhancement from the SIL is quantified by fitting the photon counting measurement using a saturation function as derived in Eq.3.7. The fit to the data reveals an intensity at infinite pump power without and with the SIL of 121 $\pm$ 3 and 520 $\pm$ 10 kcps respectively. This represents a $4.3 \pm 0.1$ fold enhancement in the collected fluorescence. The discrepancy between the simulated and measured CE enhancement can be due to a number of factors. The complex growth procedure and coalescing sample planes results in a rough surface sample. Whilst the Meltmount may act to smooth the surface imperfections, and imperfections on the bottom surface of the SIL, the rough interface scatters/refracts light away from the collection optics. The surface roughness was not accounted for in the simulations. The reflection due to the index contrast between the semiconductor and Meltmount was not included in either the analytical or numerical determination of the collection efficiency. The chromatic aberration of the $NA = 0.75$ objective limits the overlap of the excitation and collection PSFs. This is reflected in the similar saturation pump powers; 0.98 $\pm$ 0.05 and 0.60 $\pm$ 0.03 mW with and without the SIL, respectively. Using a more apochromatic lens therefore may lead to higher CE enhancement factors with lower pump powers.

### 5.4 Evanescent-Field Enhanced Collection Efficiency

In the previous experiment, a $NA = 0.75$ lens was chosen to match the critical angle of TIR. Due the sample surface morphology and properties of the adhesion material, precise control over the thickness of the adhesion layer between the SIL and semiconductor was impossible. However, the application of an adhesive layer was necessary in order to avoid the formation of an air gap. Assuming a finite air gap, the critical angle for TIR $\theta_c = \sin^{-1}(n_{\text{Air}}/n_{\text{GaN}}) = 28^\circ$. In this experiment, the impact of the polymer spacer layer is investigated by considering emitters in AlN. Using numerical FDTD simulations, a dependence of the CE due to the thickness of the adhesion polymer is determined
Figure 5.9: Hemispherical SIL enhanced collection efficiency. i) CE enhancement of a hemispherical SIL as a function of the emitters dipole azimuthal angle $\phi$. ii) Measured power-dependent intensity with (blue) and without (green) a hemispherical SIL for the emitter SEREN1.

at high numerical apertures. This dependence is accredited to coupling the formed evanescent field through the polymer layer. The evanescent coupling is experimentally investigated using statistical analysis over more than 500 emitters in three AlN samples using a fully automated process.

5.4.1 Spacer Thickness Dependence on Collection Efficiency

In order to investigate the impact of the adhesion layer with regards to the CE one can return to FDTD simulations. The simulation environment was setup as previously described in Chapter 4.1.1. The thickness of the polymer PMMA ($n_{PMMA} = 1.5$) is swept in the simulation environment from 500 nm to direct contact between the SIL and the semiconductor. The simulation results are shown in Fig.5.10. The numerical simulations reveal a dependence of the CE on the polymer thickness and NA of the collection optics. The greatest gain in CE can be made by combining a high NA lens with a thin PMMA layer. The CE for a NA of 0.9 as a function of the polymer thickness is presented in Fig.5.10 (ii). The dependence on the polymer thickness can be understood considering TIR. TIR occurs at incidence angle above that of the critical angle, $\theta_c$, where, due to Snell’s law,

$$\theta_c = \sin^{-1}(\frac{n_{PMMA}}{n_{AlN}}) = 44^\circ. \quad (5.4)$$

The numerical aperture in the semiconductor is unchanged due to the intermediate polymer layer:

$$\frac{n_{PMMA}}{n_{SIL}} = \frac{N_A_{SIL}}{N_A_{PMMA}}. \quad : \quad N_A_{AlN} = N_A_{PMMA} \frac{n_{PMMA}}{n_{AlN}} = N_A_{SIL} \frac{n_{PMMA}}{n_{SIL}} = N_A_{SIL} \frac{n_{SIL}}{n_{AlN}}. \quad (5.5)$$

Considering the NA in the semiconductor is unchanged, the loss of CE at high numerical apertures is accredited to TIR between the semiconductor and polymer. Considering $\theta_c$ and converting the angle to an effective NA, $N_A_{Ce} = \sin(\theta_c) = 0.69$. The analysis is supported in Fig.5.10 where for NA > 0.7
and polymer layers thicker than 200 nm the CE is constant. The thickness dependent CE for thinner polymer layers can be understood by considering the evanescent field formed at the interface.

It is well understood that TIR leads to a solution to Maxwell’s equations that includes a stationary wave component which exponentially decays away from the interface - an evanescent wave. When a secondary interface is placed in proximity to the evanescent field, approximately less than one wavelength from the interface, the TIR becomes frustrated and light can couple through the medium between the two interfaces. Coupling the light through the polymer converts the evanescent field to a propagating wave. The propagating wave can be collected by the imaging optics. This is known as frustrated total internal reflection. Evanescent fields in this form are described by the following expression,

\[ E(z) = E(s)e^{-z/d}, \quad \text{and} \quad d = \frac{\lambda_0\mu_{AlN}}{2\pi\sqrt{\left(\frac{\mu_{AlN}}{\mu_{PMMA}}\right)^2 \sin^2(\theta) - 1}}, \quad (5.6) \]

where \( E(z) \) is the electric field parallel to the interface, \( E(s) \) is the electric field at the interface, \( \theta \) is the angle of incidence of the light, \( \lambda_0 \) is the wavelength of the light in a vacuum and \( d \) is the penetration depth of the evanescent field. Due to the angular dependence of the coupling through the polymer, one can consider the two limiting angles, just beyond the angle of TIR, \( \theta_{TIR} = 45^\circ \), and the acceptance half angle of the imaging system, \( \theta_{NA} = 64^\circ \). The penetration depths as determined using Eq. 5.6 are given as \( d_{TIR} = 191 \) nm and \( d_{NA} = 38 \) nm, respectively. The determined penetration depths are consistent with the simulated thickness dependent CE in Fig. 5.10. For film thicknesses below \( d_{TIR} \) the CE is increased above the asymptotic value at infinite polymer thickness.
5.4.2 Statistical Experimental Technique

The rough surface of the previously investigated Seren sample presents a practical problem associated with the controlled application of thin polymer layers. In contrast, the off-the-shelf AlN epilayer presents a smooth sample surface. In this experiment, three samples are used. SP1 is a bare 1 µm AlN epilayer without any applied polymer or SIL, representing a baseline measurement. SP2 and SP3 were spun with A4 950K and A2 450K PMMA, with a measured film thickness of 212 and 70 nm, respectively. The PMMA film thickness was measured using an ellipsometer. Two SILs are polished and transferred onto samples SP2 and SP3 respectively using the process illustrated in Fig. 5.4. No metallic markers were applied to the sample and the SILs were not deterministically placed. Instead, a statistical analysis is performed, that measured more than 500 emitters across the three samples.

Power dependent photon counting measurements were taken sequentially over a large number of emitters using a fully automated routine. Confocal scan maps were measured revealing the presence of emitters in the AlN epilayer. To avoid selection bias, due to the linearly polarised nature of the 532 nm laser used to excite the emitters, three scans maps were taken with the polarisation angle rotated in the plane of the sample. This avoided pre-selecting emitters aligned to the laser polarisation. Polarisation angles of 0°, 60° and 120° were scanned in order to address the full polarisation plane assuming linearly polarised dipole emitters. The linearly polarised nature of the emitter in AlN was demonstrated in Chapter 3.2.3. Sample scan maps are shown in Fig. 5.11. It is apparent from the combined scan map in (iv), where the pixel intensity from images (i-iii) have been averaged, that pre-selecting emitters has been avoided.

The resultant scan map was then fed into an algorithm that finds the exact locations of emitters in the following manner. Initially, the scan map was analysed to remove shot noise using a 3 × 3 pixel median filter. A maximum and minimum threshold was used to avoid excessively bright (> 2 Mcps) and dim features respectively. The image was further “smoothed” using a convolution of a two-dimensional Gaussian function, with a FHWM=0.6 µm to match the expected spot size for diffraction limited imaging of a point emitter, so that there was a high probability that a single pixel is at the PSF local maxima. The smoothing further reduced the likelihood that multiple locations were not selected with the PSF due to blinking or other artefacts. A fast pixel-by-pixel analysis technique then located potential emitter locations based on the intensity of neighbouring pixels. The 126 emitter locations identified in scan map Fig. 5.11 (iv) by the algorithm are illustrated in (v). It can be observed that the algorithm overestimates the number of emitters in the scan map and occasionally selects features that are smaller than the expected diffraction limited lateral spot size. Therefore, a more involved fitting was done for each emitter in order to filter the emitters based on the PSFs.

For each emitter location, a 1 µm² subsection around each emitter was isolated from the original scan map in Fig. 5.11 (iv) and fit to a 2-dimensional Gaussian function. Certain fit parameters were used to filter emitter locations. Bad fits were filtered using a minimum threshold for the goodness of fit.
value $R^2$. The lateral width of the Gaussian fits were used to filter features that were smaller than the expected diffraction limited PSF of the microscope. The Gaussian X and Y widths were compared to prioritise features with a symmetric PSF. Asymmetric features were not filtered from the list due to the likely blurring of the PSF as a result of the multiple averaged scan maps with finite image drift between subsequent scans. The Gaussian fit parameters were also used to weight the emitters based on the Gaussian width, symmetry in X and Y, amplitude and goodness of fit. The fit was also used to accurately identify the centre of the emitter’s PSF. Post filtering, 92 emitters were identified in the scan map and illustrated in Fig. 5.11(vi).

Power dependent saturation measurements were then taken on each emitter sequentially using the following automated process. After the initial movement of the scanning system to the approximate emitter location, an X,Y and Z line scan was measured in order to find the maxima of the emitter’s PSF, focusing the imaging system on each individual emitter in order to maximise absorption of the excitation source. The polarisation of the 532 nm linearly-polarised excitation laser was then rotated in the plane of the sample to maximise absorption. A power dependent photon-counting measurement was then taken on each emitter, where the fluorescence was fibre coupled into single mode fibre and measured on a silicon APD. Optical filtering was used to only measure the 550 to 650 nm optical window. No polarisation optics were included in the collection path of our microscope.
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Figure 5.12: Evanescent-field assisted CE from a hemispherical SIL. i-iii) Histogram representing the fitted saturation intensity at infinite power power, $I_\infty$, for a number of emitters in samples SP1, SP2 and SP3. The polymer thickness is labelled on each plot. For the brightest emitter in SP3 (marked with a red star), the power-dependent intensity saturation curve (iv), the intensity as a function of excitation polarisation (inset in iv) and power dependent auto-correlation (v) histograms.

The number of emitters measured in SP2 and SP3 was carefully considered to ensure that a similar density of emitters were sampled per unit area, taking into account the magnification of the SIL. In total, 396 emitters in SP1 were sampled over a total scan area of $150 \times 150 \mu m$. Ultimately, 63 and 70 emitters are measured for SP2 and SP3 respectively.

5.4.3 Experimental Determination of the Thickness Dependence

The statistics taken from SP1, SP2 and SP3 are presented in Fig. 5.12. Fits to each saturation measurement were achieved using the expression as derived in Eq. 3.7. A good fit to the data for one of the emitters in SP3, labelled with a red star in Fig. 5.12 (iii), is shown in (iv). The contribution due to the background was ignored due to the high signal-to-noise ratio of 173 : 1. The measured distribution of the power dependent saturation intensity $I_\infty$ for SP1, SP2 and SP3 are shown in (i), (ii) and (iii) respectively. $I_\infty$ for each emitter in SP1 is binned with a bin width of 20 kcps. SP2 and SP3 are binned with a bin width of 50 kcps.

The mean value for the distributions in SP1, SP2 and SP3 are 68, 211 and 285 kcps, respectively. This corresponds to an enhancement factor of 3.1 and 4.2. Assuming that the mean of the distribution for SP1 represents a CE of 4.6%, as determined from the analytical model, the projected CE for
SP2 and SP3 can be estimated to be 14.3 and 19.3%. The enhancement demonstrates a thickness dependent CE, which follows the trend of the FDTD predicted enhancement in Fig.5.10. The highest detected count rate is measured for an emitter in SP3 with $I_\infty = 743 \pm 4$ kcps. Data for this emitter is shown in Fig.5.12 (iv,v). Pump power dependent auto-correlation data in (v) shows the presence of anti-bunching near time zero, in combination with longer timescale bunching at high pump powers. A fit to the $P = 4 \mu W$ measurement, not shown in the figure, illustrates the single photon purity, with $g^{(2)}(0) = 0.12$. An artefact at $\pm (8 \rightarrow 30 \text{ ns})$ is removed in the dataset caused by optical cross-talk in the interferometer.

5.5 Conclusion and Future Outlook

In this chapter, the h-SIL was explored numerically and experimentally as a means to enhance the imaging and CE of solid state emitters. Initially, the ideal hemispherical SIL was introduced, and the imaging improvement was demonstrated and quantified using a ray tracing approach. Two experiments were discussed in detail. The first demonstrated single emitter spectroscopy with and without the SIL, showing an enhancement in the imaging resolution for a sub-surface point source. Using the unique structure of the gallium nitride sample, and depth-resolved Raman and confocal spectroscopy, a lateral and axial resolution enhancement by a factor of the refractive index of the SIL and the SIL squared was demonstrated experimentally. A lateral resolution of $230 \pm 5 \text{ nm}$ was demonstrated for an imaging system with a high numerical aperture of 0.9. A theoretical axial resolution of 220 nm was inferred from typical axial line-scans of quantum emitters. The increased photon CE was discussed numerically and experimentally, with a good agreement between experiment and simulations. Ultimately, an enhancement factor of 4.3 was measured for a dipole with a finite out-of-plane orientation.

The second experiment exploited a statistical approach to determine the impact of the thickness of the spacer between the lens and the AlN sample. In this experiment, different polymer thicknesses were spun onto two AlN samples and the properties of over 500 emitters were used to build a distribution of the power-dependent photon emission rates using a fully automated measurement technique. A dependence on the polymer thickness was observed experimentally, which was attributed to frustrated total internal reflection at the semiconductor-to-polymer interface. The coupling of the evanescent field through the polymer was supported numerically using a finite different time domain technique. Ultimately, an enhancement factor 4.2 for a SIL with a spacer thickness of 70 nm was demonstrated, in good agreement with the predicted evanescent-field coupling assisted CE enhancement.
Chapter 6

Deterministic Photon Collection Enhancement

6.1 Introduction

In this chapter, an in-situ lithography process is proposed to deterministically enhance the amount of light collected from AlN quantum emitters. The proposed process exploits the energy-dependent absorption of light in a positive-tone photoresist to deterministically pattern photonic structures aligned to quantum emitters pre-located in a sample. We start by discussing the bi-layer lithography process that enables the transfer of the pattern into the semiconductor.

6.1.1 The Bilayer Lithography Process

To enable the patterning of photonics structures into a 1µm AlN-on-sapphire substrate a bilayer photolithography process was proposed. The process operates on the principle that one can transfer a pattern into a semiconductor by depositing a metal film which acts as an etch mask during reactive ion etching (RIE). Fig 6.1 illustrates the proposed process in detail. The process starts in (i) with a semiconductor-on-substrate sample that has been removed of surface contaminants using solvent and oxygen plasma cleaning. A bilayer resist stack is then applied in (ii), using a spin coating technique. Spin coating achieves uniform film thicknesses across the sample, excluding the unavoidable beads formed at the edge. The photosensitive resist, S1805, was selected due to its availability, viscosity and sensitivity to the 405 nm laser used to define the pattern. The exposure wavelength was selected to operate within the optical window of the optics used in the room temperature microscope introduced in Chapter 2.1.1. The corresponding LOR3A undercut resist was selected due to its viscosity and solubility. Both resists are deposited with a layer thickness of 600 nm to enable the deposition of thick metal layers. After spin coating, the sample is patterned with the high-energy (405 nm) laser in (iii) to
define the pattern. Emitter locating was achieved prior to application of the bilayer resist stack. The locations of emitters are relative to alignment marker features as described in Section 6.3. Application of the laser leads to a polymerisation of the exposed resist which can subsequently be dissolved in a solution referred to as the ‘developer’. The S1805 resist is a positive tone resist. Therefore, the exposed resist is soluble to the developer, revealing the substrate. The solubility of the S1805 and LOR3A films results in an undercut in the LOR3A layer that aids in removal of the resist post mask deposition. The undercut profile is illustrated in the figure post-development in (iv).

The developed resist stack is then deposited with a 100 nm Nickel film in Fig.6.1(v) to define the etch mask. The undercut decouples the metal from the resist stack, avoiding tearing the metal during subsequent solvent removal of the bilayer resist stack in (vi). This motivates the use of a bilayer resist stack as opposed to a single photoactive resist layer. The sample is loaded into an inductively coupled plasma (ICP) RIE chamber to transfer the pattern into the semiconductor. A BCl$_3$/Cl$_2$ chemistry selectively etches the semiconductor in (vii) to a depth defined by the etch time. At this stage, the metal mask can be removed using an acid etch to reveal the vertically defined pattern. One could additionally reload the sample into the RIE chamber with a Faraday cage to achieve angled etch features. The Faraday cage has been shown to change the impinging angle of ions accelerated towards the sample due to the electromagnetic screening properties of the cage [196], [217]–[219], creating an undercut etch profile that is geometrically determined from the cage design.

6.1.2 Lithography Microscope

To facilitate the deterministic enhancement of III-nitride quantum emitters, modifications were made to the room temperature microscope as introduced in Chapter 2.1.1. An additional 405 nm beam was introduced in the excitation path, which acts to spatially overlap the 405 nm laser to the 532 nm excitation and the collection beam path. The excitation and lithography beam path is illustrated in the dashed box in Fig.6.2. The lithography beam path was incorporated in the system using the dichroic beamsplitter DM1. Alignment of the lithography laser with the excitation beam path was achieved independently using mirrors M1 and M2. Mirrors M3 and M4 enable overlapping the aligned excitation and lithography beams with the collection beam path, controlled with mirrors M9 and M10. The optical filters F1 and F2 act to clean up the lithography and excitation lasers, respectively. F3 acts to suppress the reflection from the fluorescence.

Using the dual-axis galvanometric mirror (M5) and the optical 4f system, one can simultaneously scan the excitation, lithography and collection beam paths. This enables the patterning of photonic structures with feature sizes close to the diffraction limit of the lithography source. An example of a test exposure using the lithography system, which demonstrates optical features down to 600 nm using the 405 nm lithography laser, is shown in Fig.6.3. The exposure time was varied using a solenoid shutter in the beam path. Vibrations due to actuation of the solenoid were avoided by using out-of-
Chapter 6. Deterministic Photon Collection Enhancement

Figure 6.1: Illustration of the top-down lithography process developed to deterministically enhance the photon detection rate from III-nitride quantum emitters. i) Semiconductor-on-substrate sample stack. ii) Photo active resist bilayer spun onto the sample. iii) Exposure of the resist stack with a 405 nm laser. iv) Resist development. v) Metal deposition vi) Lift-off process. vii) ICP-RIE dry etch to create vertical sidewalls. viii) Faraday cage assisted dry etch for undercut side facets. ix) Resultant undercut profile from the angled ICP etch. The metal mask is removed using an acid etch reveals the photonic structure.

Figure 6.2: Illustration of the adapted confocal microscope used for deterministic patterning of photonic structures around quantum emitters. Mx - Mirrors, Lx - Lens, Fx - Optical filter, DMx - Dichroic Mirror, BSx - Beamsplitter and SMF - single mode fiber.
Chapter 6. Deterministic Photon Collection Enhancement

fiber beam blocking, as illustrated in Fig. 6.2, separate from the microscope. A SMF-coupled 405 nm
laser diode is collimated using a fixed-focus collimation package FCP\textsubscript{1} and passed through the solenoid
shutter before being coupled back into SMF via FCP\textsubscript{2}. The solenoid is switched with a controller that
is capable of pulsed actuation of the shutter. This mode is used for all single pixel exposures to pattern
micro-pillars due to the accurate timing, with ±0.3 ms accuracy at the minimum exposure time of
15 ms.

The exposure dose required to polymerise the resist is estimated in the following manner. We start by
considering the focal spot size using a NA = 0.9 lens. According to the Rayleigh criterion the smallest
spot size is,

\[ \text{FWHM} = 0.51 \frac{\lambda}{\text{NA}} = 230 \text{ nm}, \quad (6.1) \]

where \( \lambda = 405 \text{ nm} \). The FWHM value is converted to the Gaussian beam waist radius \((1/e^2)\) in the
following manner,

\[ w_0 = \frac{\text{FWHM}}{2\sqrt{2\ln(2)}} = 97.7 \text{ nm}. \quad (6.2) \]

The entrance pupil of the objective acts as an aperture with radius \( r \) that reduces the power through
the objective \( P_0 \) in the following form,

\[ P_0(r) = P(\infty) \left( 1 - \exp\left( -\frac{2r^2}{w_e^2} \right) \right), \quad (6.3) \]

where \( P(\infty) \) is the measured power before the lens. To determine \( P_0(r) \) we first determine the beam
waist of the \( \lambda = 405 \text{ nm} \) laser when collimated from a SMF fiber with MFD = 3.3 \( \mu \text{m} \) by a lens with
focal length \( f = 16.5 \text{ mm} \):

\[ w_e = \frac{2\lambda f}{\pi \times \text{MFD}} = 1.43 \text{ mm}. \quad (6.4) \]

Considering an objective lens with effective focal length \( f_e = 1.65 \text{ mm} \) the pupil radius \( r = f_e \times \text{NA} =
1.485 \text{ mm} \). This corresponds to a filling factor \( w_e/r = 0.96 \). For the filling factor of 0.96 the power
through the aperture has fallen to 88\% the initial power. One can now estimate the power density
by normalising the power at the focus by the area of a circle with radius equal to the beam waist \( w_e \),

\[ P_d = \eta(\lambda) \times \frac{2P(r)}{\pi w_e^2} \left[ \frac{\text{W}}{\text{m}^2} \right], \quad (6.5) \]

where \( \eta(\lambda) \) represents the wavelength dependent transmission through the objective taken from the
manufacturer’s datasheet. The final consideration is to convert the units to Joules by multiplying by
the exposure time \( t \). These expressions present the ideal case for a perfect focusing lens. The optical
density and therefore exposure dose is often over-estimated due to the chromatic performance of the lens. Therefore, exposure dosage tests were used to more accurately determine the required exposure time. An example of an exposure dose pattern that is subsequently etched into the semiconductor is shown in Fig.6.3.

### 6.2 Periodic Arrays of Pillars Coupled to Randomly Position Emitters

To investigate the experimental enhancement of the light collected from a micro-pillar, periodic arrays were patterned on a 1 μm AlN-on-sapphire sample. The exposure dose and therefore pillar size is varied across the pattern with exposure times between 10 and 250 ms. The pattern transfer is illustrated in Fig.6.3 from inception in the software (i) to the final etch in the semiconductor (iii) via the transfer of the pattern into the resist bilayer (ii). The post-etch profile of the pillars can be observed in the SEM micrograph in (iv). It is worth noting the non-isotropic edge facets of the pillars in the etch, which presents a discrepancy with respect to the simulated collection efficiency in Chapter 4.4.1. Post processing of the pillars using a chemical etch such as potassium hydroxide (KOH) selectively etches the vertical c-plane leading to vertical side profiles [220]. A second pattern, not shown in the figure, varied the exposure dose from 50 to 250 ms. The markers and lettering were exposed using a pixel-by-pixel approach where the scanning system is displaced with a finite step size and a finite exposure time at each pixel. Typical values for the step size and exposure time are 0.2 μm and 30 ms respectively.

Confocal scan maps around a 10 × 10 array of pillars, patterned with an exposure time of 30 ms, are shown in Fig.6.4(i). The confocal scan maps, plotted with a log colour scale, illustrate the outline of the pillar array with a number of pillars hosting emitters. The sample was etched using ICP-RIE to a depth of approximately 800 nm. The etch depth was determined by in-situ laser interferometry on a similar sample. The image is processed using the emitter locating algorithm as described in Chapter 5.4.2. The determined emitter locations are illustrated in Fig.6.4(ii). A number of observations can be made from the scan images and the emitter locations. Emitters only occur on either the pillars or on the unetched markers, the four crosses at each corner of the array. The lack of features between the pillars and the determined etch depth suggests that the emitters are located at least 200 nm away from the AlN-to-sapphire interface. In the future, controlled etch depths could be used to more accurately determine the depth of the emitters.

Out of the 100 pillars in the array only 38 were selected by the automatic emitter finding algorithm. Out of the 38 selected, many show linear power-dependent behaviour and as such exhibit high saturation pump powers. By considering only emitters with a saturation pump power lower than 1 mW it can be determined that 10 pillars host emitters. Out of the 10 emitters, a number show high intensity photon emission rates. A saturation and second-order correlation measurement for one of
Figure 6.3: Demonstration of the proposed lithography system. i) Exposure dosage test where arrays of single pixels are exposed with varying exposure times from 10 to 50 ms as defined in the software. ii) Optical image of the developed resist stack after exposure of the pattern in (i). iii) Scanning electron micrograph of the transferred pattern etched into the semiconductor. iv) Angled scanning electron micrograph of the pillar profile.
6.3 Deterministic Patterning of Micro-Pillars Spatially Aligned to Emitters

To enable the deterministic patterning of photonic structures aligned with randomly positioned quantum emitters an alignment marker based positioning process was proposed. The process is illustrated in detail in Fig. 6.5. The technique exploits the deposition of alignment markers to pre-
determine emitter locations with respect to the markers. The process starts with the deposition of metallic markers on an AlN sample. 100 nm of Nickel is deposited onto the sample in (ii) using a mask-less photolithography technique. A confocal scan map, taken with a dichroic imaging system in (iii), reveals the position of emitters relative to the markers. The dichroic imaging system, as illustrated in Fig.6.6, was designed based on the intuition that using X number of detectors would enable measuring X number of confocal images at the same time. As illustrated in Fig.6.6, both the reflection and fluorescence images can be measured concurrently, which reduces the error associated with successively measuring the reflection and the fluorescence. Measurement of the reflection map at this stage reduces the error associated with projecting the emitter locations onto the sample during the lithography.

Once both the fluorescence and reflection maps have been taken in Fig.6.5(iii) the sample can be prepared for the lithography. The bilayer resist stack of LOR3A and S1805 is spun onto the sample in (iv). The alignment markers are scanned with an attenuated 635 nm laser to reveal the position of the alignment markers in (v). The wavelength and low power of the reflection laser avoids polymerising the resist. The reflection map taken in (v) is compared to the reflection map taken in (iii) to account for
any translation and rotation of the sample using a computer vision based approach. The algorithmic translation of the reflection maps utilises the pixel intensity to align features with a similar shape. Whilst the alignment markers are often visible in fluorescence maps, due to imperfect filtering of the laser reflection from the metallic markers, the fluorescence signal dominates by design. This reduces the algorithms ability to align the two images. This motivates the use of the dichroic imaging system to concurrently measure the reflection as well as the fluorescence in (iii).

On successful alignment of the two reflection maps, the algorithm projects the locations of emitters from the fluorescence map in Fig 6.5(ii) onto the reflection map taken with the resist stack in-situ in (v), as illustrated in (vii). The emitter locations can then be directly patterned with the 405 nm laser to expose a pattern on or around the emitters. In the context of patterning micro-pillars on top of the emitter locations, development of the resist in (viii) reveals the emitters. Nickel is then deposited in accordance with the process described in Fig 6.1(v-vii). Post etch, only the pre-selected emitters and alignment markers remain, where the emitters are embedded in the centre of the pillar.

### 6.3.1 Dichroic Imaging

The out-of-fiber dichroic imaging is achieved in the following manner. The fluorescence and reflection signal are coupled into SMF using the confocal microscope in Fig 6.2. All filters, excluding the dichroic mirror DM2, are removed from the system. The reflection and fluorescence signal is then coupled out of the fiber using a metallic reflective collimator. The collimated beam is split on a dichroic beamsplitter with a long pass cut-on wavelength of 550 nm. The fluorescence transmits through the beamsplitter with additional optical filtering to measure only the 550 - 650 nm optical window. The optical window overlaps with the emission wavelengths of the AlN emitters as determined in Chapter 3. The fluorescence is then coupled into multi-mode fiber (MMF) using a fiber collimation package with anti-reflection coatings across the visible spectrum. Coupling into MMF reduces the precision of the alignment required to couple the light into the fiber due to the increased core size of 50 µm. Therefore, aligning the coupling is done using a coarse XY and tip-tilt stage holding the collimation package and fiber. The reflection is handled in a similar manner, with the only difference being the inclusion of a manual attenuator to avoid over exposing the detectors. The system is inherently flexible by design, where all the filtering and the dichroic mirror can be swapped out.

A demonstration of the resultant fluorescence and reflection image from an AlN sample is shown in Fig 6.6(ii) and (iii), respectively. It is apparent in (ii) that the alignment markers are visible in the scan map due to the finite reflection signal through the optical filtering. One can observe how the fluorescence-to-reflection ratio in the image is low. The low contrast reduces the probability of accurate alignment via the computer vision algorithm. In contrast, the reflection scan image in (iii) illustrates the metallic marker image with a high signal-to-noise ratio. The reflection scan before and after resist deposition can now be used to translate emitter locations for the lithography.
Figure 6.6: Illustration of the dichroic imaging technique used to split the reflection and fluorescence images for the computer vision based alignment. i) Illustration of the out-of-fiber dichroic splitting of the fluorescence and reflection. ii) Example fluorescence confocal image of a sample with metallic alignment markers, measured on APD2 in (i). iii) Concurrent reflection scan map measured on APD1 in (i).
Chapter 6. Deterministic Photon Collection Enhancement

Figure 6.7: Uncertainty in location to position of emitter in AlN. i) Subsection of a confocal scan map revealing the location of an emitter. Y (ii) and X (iii) cross-sections of the scan map in (i) across the emitter. Both cross-sections are fit with a Gaussian function. iv) Histogram of the uncertainty in position taken from a two-dimensional Gaussian fit to 281 emitters.

6.3.2 Uncertainty in Emitter Positioning

To quantify the uncertainty in positioning emitters with the microscope, 281 AlN emitter locations were extracted from multiple confocal scan maps. The $X_c$ and $Y_c$ centre points are taken from the Gaussian fits and the fit uncertainty represents the uncertainty in positioning the emitter. Data for a representative emitter is shown in Fig.6.7(i-iii). Cross-sections in Y (ii) and X (iii) were extracted from the image in (i). The fit to the data reveals $X_c = 11.889 \pm 0.006$ and $Y_c = -2.08 \pm 0.01 \mu m$. This represents an uncertainty in locating the emitter of 6 and 10 nm, respectively. A histogram showing the uncertainty in locating the 281 emitters is shown in Fig.6.7(iv). The data is binned with a bin width of 5 nm. The distribution is fit with a log-normal distribution and the centre of the distribution is given as $19.0 \pm 0.2 \text{ nm}$. The uncertainty in determining the location of emitters with the confocal microscope is therefore at least an order of magnitude smaller than the diffraction limit of the excitation laser. In principle, one could exploit a SIL as explored in Chapter 5 to determine the location of emitters with an improved uncertainty.
To illustrate the alignment marker based emitter locating and patterning process a proof of concept measurement was taken. For the measurement, the same alignment markers were imaged with the dichroic imaging system with a finite rotation and translation between scans. The reflection images, with their real world coordinates, are illustrated in Fig. 6.8(i). The left hand side map (green) represents the scan taken to reveal the position of emitters with respect to the markers, map (iii) in Fig. 6.5. The right hand side map (blue) in Fig. 6.8(i) represents the reflection map taken with the resist stack in-situ, illustrated in Fig. 6.5.(v). By measuring both the reflection and fluorescence for both images one can quantify the accuracy of the computer vision based alignment approach. The fluorescence images are shown in (iii) and (iv,v) for the emitter finding and pre-lithography stages of the process, respectively. Fig. 6.5(v) directly compares the projected emitter positions taken from the computer vision based alignment algorithm to the measured emitter locations with the finite sample displacement and rotation. An illustration of the computer vision based alignment is shown in (ii). One can observe that the algorithm was able to overlap and align the two images.

To quantify the accuracy of the image alignment algorithm 50 emitter locations were selected in the fluorescence scan map shown in Fig. 6.8(iii). The 50 emitter locations are determined using a combination of manual selection of the location coupled with the more accurate Gaussian fitting of the PSF. The 50 emitter locations were then translated using the translation matrix output from the alignment algorithm. The projected emitter locations are shown on the reflection (iv) and fluorescence (v) scan maps in the figure. Directly comparing the projected coordinates with the emitter locations on the fluorescence map in (v) enables quantifying the accuracy of the alignment.

A statistical analysis of the accuracy is illustrated in Fig. 6.9. The displacement between the projected emitter locations and the fit emitter locations was determined by fitting each emitter to a two-dimensional Gaussian function and extracting the XY coordinates. The displacement in X and Y is binned into a histogram with a bin width of 25 nm, illustrated in Fig. 6.9(i). The histogram demonstrates that the alignment was more accurate in X than in Y. 12 emitter locations are displaced in X less than 25 nm from the real emitter location as compared to 5 in Y. The maximum displacement \( \Delta Y = 570 \text{ nm} \) and \( \Delta X = 240 \text{ nm} \). On close inspection of the projected emitter locations in Fig. 6.8(v) one can observe that the misalignment is dependent on the radial distance. The displacement in X follows a less pronounced radial dependence. The radial misalignment, and as such the large displacements observed in the data, can be avoided by ensuring a smaller rotation than the 30° misalignment in the proof-of-concept measurement. In the future, different alignment markers with better defined features will likely reduce the observed displacements between the projected and
Figure 6.8: Alignment based lithography proof of concept. i) Two reflection scans over the same alignment markers with a finite translation and rotation between scans. The blue scan map (right side) represents the reflection scan as taken with the resist stack in-situ. ii) Aligned reflection maps using the computer vision based algorithm. iii) Fluorescence map with 50 emitter locations highlighted. iv,v) Projected emitter locations on the reflection (iv) and fluorescence (v) maps. The fluorescence map was measured concurrently to quantify the projection accuracy.
6.3.4 Deterministically Patterned Micro-Pillars

To demonstrate the deterministic patterning of photonic structures an AlN sample was patterned with alignment markers and scanned with the dichroic imaging system to reveal the location of emitters in the sample. The fluorescence scan map is shown in Fig.6.10(i). 16 emitter locations are selected in the scan. Emitters close to the centre of the scan were preferentially selected. The sample was etched using a BCl$_3$/Cl$_2$ chemistry in an ICP-RIE. A SEM micrograph is shown in (ii). The etched pillars can be observed in the SEM image (ii) as well as the fluorescence (iii) and reflection (iv) image. It is apparent in the fluorescence scan, which is plotted with a log colour scale, that no emitters are located within the pillars. This is attributed to aberrations in the imaging system focusing the 405 nm laser to the same location as the 635 nm reflection laser used to map the sample. In the future this can be mitigated by either using a different objective lens or using a different exposure laser. One could expose the resist using the same laser to map the reflection. This inherently avoids the requirement for spatial alignment of the reflection and exposure lasers at the cost of reduced resolution.

6.4 Conclusion and Future Outlook

To conclude, a deterministic lithography technique was introduced that was designed to enhance light collection from pre-determined emitters. To enable such a process, adaptations were made to the room temperature confocal microscope to enable spatially overlapping a 405 nm laser to the excitation arm. Test patterns were written that demonstrated exposure resolutions down to 600 nm using a 405 nm diode laser on a bilayer resist stack. The test patterns were measured optically to determine both the enhancement in light and the probability of stochastically enhancing an emitter. The enhancement in
Figure 6.10: Deterministic patterning of photonic micro-pillars. i) Confocal scan map around alignment markers with selected emitter locations highlighted. ii) Tilted scanning electron micrograph of the etched pillars. iii,iv) Confocal fluorescence (iii) and reflection (iv) maps of the alignment markers post etch. The fluorescence map is plotted using a log colour scale.
light collection was compared to a statistical analysis over 400 sampled emitters taken from Chapter 5. A collection efficiency enhancement of $\times 13$ was determined for the brightest emitter using power-dependent photon counting measurements.

A process to deterministically pattern photonic structures was proposed. The technique exploited metallic markers pre-deposited on the sample surface to determine the location of emitters. A dichroic imaging system was developed, where both the fluorescence and reflection from the sample can be concurrently measured. A proof-of-concept measurement quantified the accuracy of the a computer vision based alignment algorithm to align independent scan maps. A radial dependence on the accuracy was observed which was attributed to the finite rotation of the images. The error can be mitigated by minimising the rotation between the pre-scanned reflection/fluorescence and pre-lithography reflection maps. In the best case, 12 emitter locations had an error in displacement below 25 nm in X with 5 in Y.

Ultimately, 16 emitter locations were deterministically patterned using the 405 nm laser. Confocal imaging of the sample illustrated that none of the pillars contained emitter post etching. The misalignment is accredited to chromatic aberrations associated with focusing the 405 nm laser to the same location as the 635 nm reflection laser. However, the proof-of-concept exposure demonstrates the applicability of using the confocal microscope with the dichroic imaging system for direct enhancement of quantum emitters in the III-nitrides.
Chapter 7

Discussion and Conclusion

In this thesis, the III-nitride family was explored as a material platform for practical quantum photonics. To this end, GaN and AlN were explored using confocal microscopy to probe the optical properties of photo active emitters. Bright room temperature emission was discovered in both GaN and AlN, spanning across the visible spectrum. To discuss the properties of the emitters in more detail, we consider AlN and GaN independently below.

Quantum emitters in AlN were discovered and explored in this thesis as an antibunched photon source. Confocal microscopy revealed bright emission from localised point-like emitters. Spectral measurements demonstrated a wide phonon contribution to the spectra spanning over 200 nm at room temperature. The broadening is attributed to coupling to phonons with specific phonon replicas identified for a representative emitter AlN1. The coupling to phonons is discussed in terms of the Franck-Condon principle, where the coupling probability is governed by the wavefunction overlap between the ground and excited state vibrational levels. The coupling is detrimental for any quantum emitter, as interactions with phonon modes acts to de-phase the coherence of the emitter and broaden the linewidth. Interactions with phonons is unavoidable at room temperature. To mitigate the interaction with phonons, the AlN sample was cooled to 4 K using a closed-loop cryostat. The temperature dependence on the spectrum for emitter AlN1 was recorded and fit using a Voigt fitting function. Extracting the Gaussian and Lorentzian linewidths from the Voigt function enabled identifying the broadening processes as a function of the temperature. The temperature dependent broadening was attributed to homogeneous broadening with the $E_{2\text{LOW}}$ optical phonon mode, determined by fitting the temperature dependence of the Gaussian and Lorentzian linewidth with a Bose-activated function to determine the activation energy of the broadening. The activation energy agreed with the energy of the $E_{2\text{LOW}}$ vibrational mode. At low temperatures, it was determined that the broadening of the linewidth was due to inhomogeneous spectral wandering of the emission energy. This was explored using time-resolved spectral measurements, with a measurement integration time of 2 s.

It was determined in the time-dependent spectral measurements that the CCD used was not sensitive
Chapter 7. Discussion and Conclusion

enough to probe the dynamics on faster timescales. It was suggested that one could use photon-counting measurements to overcome the limitations of the CCD. The measurement principle is as follows. Spectral filtering splits the ZPL onto two detectors, with the lower energy side on detector one and the higher energy side on the other detector. As the ZPL changes energy, for example the ZPL loses energy, the spectral filtering directs the photons onto the first detector. Contrarily, if the ZPL gains energy then the photons are measured on detector two. The time varying intensity on the two detectors due to the wandering of the ZPL materialises as a bunching of the photon statistics, which can be observed measuring the second order correlation function. The timescale of the bunching is directly related to the timescale of the spectral wandering. This technique was exploited for GaN quantum dots to measure the longest coherence measured to date for a nitride quantum emitter, with a spectral diffusion timescale of $1170 \pm 50$ ns [67]. In the future, this technique could be exploited for AlN and GaN emitters to probe the timescale of the spectral wandering on pico/nano second timescales.

Measurement of the absorption and emission polarisation of the emitters in AlN demonstrated interesting properties. By independently measuring the absorption and emission polarisation of the emitter AlN1 the cross-polarised nature was determined. The polarisation was attributed to the formation of two cross-polarised dipoles in the emitter. Absorption occurs on one dipole where a fast non-radiative transition preferentially relaxes the emitter to the cross-polarised dipole. One interesting prospect of such a system is the efficient pumping and photon collection. Using a cross-polarised excitation and collection scheme, one could pump the emitter and suppress the laser reflection without the need for optical filtering. This could enable a number of interesting measurements. One could tune the excitation wavelength of the laser to match the energy of the absorption dipole. Assuming that the preferential decay of the absorption dipole is faster than the stimulated emission lifetime then the system would relax into the emission dipole and spontaneously emit a photon. This would overcome the 50% collection efficiency upper bound for cross-polarised excitation and collection of quantum emitters without a cavity [34]. If one considers the resonant excitation of the emitter using a narrow linewidth excitation laser, then a resonant measurement in this manner could enable probing the spectral wandering. A time-dependent intensity would be observed as the emitter wanders on and off resonance with the excitation laser. If one assumes that on resonance emission leads to vertically polarised light and off resonance excitation leads to horizontally polarised light, due to the normal excitation and collection dipoles, one can see how the time-dependent cross polarised emission can be measured on two detectors using polarisation beam splitting.

A tunable excitation source can enable measuring the energy dependent absorption properties of the quantum emitters. By detuning the laser across the low energy side of the ZPL one can collect the photons emit into the ZPL and high energy PSB. When the defect is efficiently excited, for example when the laser energy is equal to the energy of a phonon assisted transition, the defect
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will radiate with an increased number of photons per second. The probability of photon absorption as a function of the laser wavelength is governed by the Franck-Condon principle and mirrors the probability of photon emission. One can use the absorption measurement to accurately determine the interactions with phonon modes at high and low temperature, enabling more efficient and pseudo-resonant excitation of the emitters’ energy level structure. In addition, detuning the excitation source may enable probing the polarisation properties of the AlN emitters in more detail. Measuring the pump energy dependent absorption polarisation may enable quantifying the validity of the four level cross-polarised dipole model. As the pump energy is reduced, one would expect a threshold where the absorption dipole changes in polar angle. This can be understood considering the horizontal and vertical dipoles. Assuming that the higher energy dipole is vertically orientated, then at high pump energies the vertical dipole will be preferentially pumped. As the energy of the pump is reduced below the energy difference between the excitation and ground states of the vertical dipole then the dipole can no longer be optically excited. The horizontal dipole will subsequently be pumped and one would expect the polar angle of the absorption measurement to rotate by 90°. The energy at which the absorption polar angle changes would be equal to the energy of the vertical dipole. The energy of the horizontal dipole, assuming preferential relaxation of the carriers at low pump power into the lower energy dipole, would be equal to the ZPL energy. In this case one has measured the energy difference between the two dipoles, which may enable controlling the polarisation state of the defect using an external energy source such as a magnetic of electric field.

In addition to the quantum emitters discovered in AlN, photo-stable room temperature emitters were uncovered in a semi-polar GaN sample. Near infrared emission was discovered in a similar manner to the AlN emitters. However, spectral measurements of the emitters illustrated a more prominent ZPL with 34% of the intensity in the ZPL. The high portion of the intensity in the ZPL, often referred to as the Debye-Waller (DW) factor, is in stark contrast to the < 4% for the emitters in AlN. In addition, the PSB of the GaN emitter can be represented with a single Gaussian function with a FWHM \(\approx 40\) nm. This represents a narrower broadening as compared to the \(> 200\) nm broadening for the AlN emitter. The ZPL is best described at room temperature with a Lorentzian function with a FWHM \(= 5.62 \pm 0.07\) nm, suggesting the broadening of the ZPL is due to a homogeneous process such as phonon broadening. This is in agreement with what was observed for the AlN emitters. Temperature dependent spectra may enable quantifying the particular phonon mode that broadens the ZPL at ambient conditions. The spectral properties of III-nitride emitters uncovered in this thesis are compared to other III-nitride emitters and emitters in diamond in Fig. 7.1. The spectral width, which is defined as the energy difference between the lowest and highest energy spectral contribution, as taken from the figures in each reference, is plotted as a function of the ZPL energy for emitters in AlN [183], [184], GaN [177], [179], [221], h-BN [94], [222] and diamond [110], [223], [224]. One can observe from the plot how the GaN and AlN
Figure 7.1: The ZPL energy as a function of the total width of the spectrum for emitters in the III-nitrides as compared to emitters in diamond. The AlN, GaN$_{SEREN}$, GaN$_{Mg}$ and h-BN$_{Cardiff}$ spectra were measured in Cardiff. The h-BN spectral was measured by my colleague Reza Hekmati. All other data points are taken from the literature, where the label superscripts refer to the following reports; [a] - [183], [b] - [177], [c] - [179], [d] - [94], [e] - [222], [f] - [110], [g] - [223] and [h] - [224].

emitters explored in this thesis compare to other known room temperatures emitters in the III-nitrides and diamond. Interestingly, a general trend where the higher the energy of the ZPL transition the larger the broadening can be observed from the data.

Whilst a significant amount of information was uncovered with regards to the optical properties of the emitters in GaN and AlN, the physical origin of the emission remains elusive. Techniques such as density functional theory (DFT) simulations may in the future enable identifying the crystallographic origin of the emission. The varying emission energies of emitters within the same sample increases the complexity of the analysis. An understanding of origin of the emission may be obtained by investigating the direct growth of thin films of GaN and AlN with a controllable density of emitters.

If one were to grow a series of sample with a varying concentration of a foreign element present in the growth chamber, one may be able to observe a varying density of emitters within the samples. Controlled growth, along with DFT simulations of various atomic configurations with the foreign element, may enable identifying the atomic origin of the emission.

Beyond determining the atomic origin of the emission, the controlled growth would enable incorporating quantum emitters in more complicated photonic and optoelectronic devices. If one considers that a thin film of GaN can be reliably grown with embedded emitters, engineering the density of emitters may lead to optoelectronic devices such as lasers and LEDs. One can also consider how incorporating a low density of emitters in a PIN diode structure, where the controlled incorporation of the emitters is within the intrinsic region of the diode, could enable fabricating a room temperature quantum diode.

In Chapter 4, photonic structures such as the solid immersion lens, micro-pillar and micro-pyramid were investigated to enhance the photon detection efficiency of an emitter embedded in a high refractive
index material. To this end, a finite difference time domain simulation method was developed and the collection efficiency enhancement of the structures were compared to a dipole simulated in the bulk semiconductor. Ultimately an enhancement factor of 4.8, 13.3 and 13.7 was determined for the lens, pillar and pyramid, respectively. Whilst the greatest collection efficiency simulated was as high as 61%, only modest Purcell factors $< 2.5$ were simulated. This is attributed to the Mie scattering scheme, which exploits the index contrast to trap some of the light in the structure where the scattered light interacts with the dipole field. To improve on the Purcell factor, which is beneficial for changing the radiative lifetime of the dipole, one would need to consider more complicated optical cavities such as dielectric bullseye cavities or distributed Bragg reflector micro-pillars [34].

The primary aim of the photonic structures investigated in this Chapter was their compatibility with the lithography process discussed in Chapter 6. Therefore, the structures are primarily limited in size by the diffraction limit of the lithography laser. However, one can exploit non-linear optical processes to overcome the diffraction limit, enabling the patterning of more complicated photonic structures such as dielectric bullseyes. Non-linear lithography has become a powerful tool for patterning sub-diffraction limited features and devices [225]–[227]. The probability of polymerisation of the resist is proportional to the intensity of the light squared. If one considers a Gaussian point spread function, the square dependence on the intensity effectively narrows the point spread function for two photon absorption. In addition, the low intensities away from the centre of the PSF results in negligible absorption. This enables patterning 2D and 3D nanostructures with resolutions lower than the diffraction limit. One can consider how a two-photon lithography process can be used in the context of integrated photonics. The enhanced resolution would enable the direct fabrication of extensive waveguide networks, limited only by the displacement of the sample stage and the patterning time. One could imagine how a quantum emitter, pre-selected for desirable properties, could be coupled into the integrated network by directly patterning waveguides on-top of the emitter. In addition, the resists and polymers used for two-photon lithography are insensitive to linear absorption of photons. This may enable determining the location of emitters with the resist stack in-situ and directly patterning photonics structures around/on quantum emitters in the nitrides.
Appendix

Semi-Polar GaN Sample

The Seren sample is grown via a complicated epitaxial process, where the top-facing surface facet is along the semi-polar (11\bar{2}2) plane. An illustration of the growth is shown in Fig.A.1(i). The semi-polar surface facet is achieved using a patterned GaN sample, which is initially half a micron of m-plane GaN grown on a m-plane Sapphire substrate. A half-micron thick silicon dioxide (SiO$_2$) layer is deposited onto the first epilayer of GaN and patterned using a photolithography process into circular disks. The SiO$_2$ disks are used as an etch mask to transfer the disk pattern into the GaN layer. The sample is reloaded into a metal-oxide chemical vapour deposition (MOCVD) chamber for re-growth. The exact dimensions and size of the disks as well as the conditions in the MOCVD chamber are tailored so that growth commences from the (0001) and (11\bar{2}0) plane in a manner that (0001) overgrows the (11\bar{2}0) plane. This suppresses the [11\bar{2}0] growth and ultimately facilitates the formation of a semi-polar (11\bar{2}2) surface facet. The application of semi-polar and non-polar GaN spans that of the solid state lighting industry, where the spontaneous polarisation along the [0001] axis (c-plane) creates a Stark shift and bending of the bandstructure for quantum well devices, as discussed in Chapter 1.2.1.

Figure A.1: Semi-polar GaN sample growth and imaging. i) Illustration of the two-stage growth process that results in the semi-polar (11\bar{2}2) surface plane. ii) Confocal scan map illustrating the presence of embedded SiO$_2$ disks.


Sapphire Fluorescence

A representative background fluorescence spectrum for a GaN-on-Sapphire sample is shown in Fig. A.2. The two fluorescence lines, R1 and R2, as labeled in the spectrum, originate from the positively charged chromium impurity Cr$^{3+}$ in the sapphire. The insert in the figure illustrates the broad phonon side band of the two R lines that are difficult to filter in optical measurements.

Figure A.2: Spectral measurement showing the fluorescence lines of the Cr$^{3+}$ impurity in sapphire. The fluorescence R1 and R2 lines are labeled and the inset shows a magnified image of the sideband that accompanies the two fluorescent lines.
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