Spectroscopy of single photon emitting defects in Gallium Nitride and Diamond

A thesis submitted in fulfilment of the requirement for the degree of Doctor of Philosophy

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Certificate of original authorship

I, Amanuel Michael Berhane, declare that this thesis titled, ‘Spectroscopy of single photon emitting defects in Gallium Nitride and Diamond' has not previously been submitted for a degree nor has it been submitted as part of requirements for a degree except as fully acknowledged within the text.

I also certify that the thesis has been written by me. Any help that I have received in my research work and the preparation of the thesis itself has been acknowledged. In addition, I certify that all information sources and literature used are indicated in the thesis.

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Peer-reviewed publications not included in this thesis but contain research contributions during the PhD study:

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the intensity. The results are vital in introducing hBN for nanophotonic applications.

2) S. Choi, A. M. Berhane, A. Gentle, C. Ton-That, M. R. Phillips, and I. Aharonovich, "Electroluminescence from localized defects in zinc oxide: toward electrically driven single photon sources at room temperature," ACS applied materials & interfaces 7, 5619-5623 (2015). This study reports electrically driven defect fluorescence from Zinc Oxide (ZnO) diodes. Direct evidence of electroluminescence (EL) from the defect is provided by exciting it both by PL and later EL yielding the same spectral properties. The results entail that defects in ZnO can be further investigated to show electrically driven single photon emission.

3) S. Stehlik, L. Ondic, A. M. Berhane, I. Aharonovich, H. A. Girard, J.-C. Arnault, and B. Rezek, "Photoluminescence of nanodiamonds influenced by charge transfer from silicon and metal substrates," Diamond and Related Materials (2015).: Here NV centre in a 5 nm detonated nanodiamond is studied by varying the termination as well as the substrate. It is reported that the spectral, as well as lifetime of the NV centre, changes by varying the factors above. This result underpins the effect of surface electrostatics on the optical properties of nanodiamonds.
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Figure 5.4: Fluorescence intensity of emitter E2 as a function of excitation power. The background-corrected saturation curve (red) yields a maximum intensity of 501 kCounts/s at a saturation power of 930 μW. The $g^2$-corrected saturation curve (blue) yields a lower bound on the maximum single photon emission rate of 203 kCounts/s at a saturation power of 313 μW ............................................................................. 115

Figure 5.5: Saturation behaviours of emitters in GaN at room temperature. a) Background-corrected fluorescence intensity versus power from a representative emitter with a
ZPL at 1.818 eV, and a maximum intensity of $\sim 105 \text{kCounts/s}$ at a saturation power of 558 $\mu$W. b, c) Statistical distribution of the maximum intensity and saturation power from 8 emitters, with a mean value of $\sim(427\pm215) \text{kCounts/s}$ and $\sim(1270\pm735)\mu$W, respectively.

Figure 5.6: Power dependent antibunching characteristics of the three emitters presented in Figure 5.2 with spectral peak at 647 nm, 679 nm and 690 nm is provided in (a) (c) & (e) respectively. As shown, emitters show power dependent bunching characteristics in the three emitters.

Figure 5.7: Schematic diagram illustrating three-level optical transitions. $\kappa_{12}$ denotes transition coefficient from ground state, 1, to excited state, 2. Relaxation coefficient $\kappa_{21}$ represent spontaneous emission, whereas $\kappa_{31}$ is the metastable state, 3, populating rate coefficient and $\kappa_{31}$ is de-shelving from metastable state to ground state. The red box further illustrates an alternate pathway for intensity dependent de-shelving from state 3 to a new excited state, 4.

Figure 5.8: Power dependent single photon behaviour of the emitter. a) Measured $g^2(\tau)$ with different powers b), c) and d) show that radiative lifetime, $\tau_1$, metastable non-radiative lifetime, $\tau_2$, and scaling factor for bunching, $a$, extracted from fitting the $g^2(\tau)$ function for different powers in (a).

Figure 5.9: Power-dependent antibunching characteristics of the six emitters E1-E6. While all emitters showed power-dependent bunching behaviour, the strength of bunching
at intermediate time scales occurs at different fractions of the excitation power. The antibunching behaviours are well fitted (red curve) using second-order autocorrelation function for three-level systems. ................................................................. 122

Figure 5.10: Power-dependent properties of the decay rates $\lambda_1, \lambda_2$ and the scaling factor $a$ for the 3 emitters E1-E6 measured at room temperature. The data points (black dots) are fitted well (red lines) by considering three-level transition kinetics.............. 123

Figure 5.11: Polarization characteristics of the 3 emitters in Sample A. The polarisation measurement for emitters whose spectral characteristic is presented in Figure 5.2 (a), (c) & (e) is shown here as (a), (b) and (c) respectively. Green curves represent excitation polarisation while red represents emission polarisation....................... 126

Figure 5.12: Room-temperature polarisation spectroscopy of emitters in GaN. a) Absorption (green) and emission (red) polarisation profiles from an emitter with a ZPL at 1.818 eV, exhibiting polarisation visibilities of 34% and 79%, respectively. b) Polarization visibilities of 14 emitters showing that while the emitters are strongly polarised in emission, they show variable degrees of absorption polarisation. c) Histogram of the difference in orientation between absorption and emission polarisation................................................................. 127

Figure 5.13: Maximum absorption angles for the 14 emitters shown in Figure 5.6. a) Scatter plot of the maximum absorption axis of the 14 emitters. b) Fundamental lattice directions of the wurtzite unit cell, showing that the maximum in angular distribution in (a) corresponds to the $[1\bar{1}00]$ lattice direction of wurtzite GaN......................... 128
Figure 5.14: Fluorescence time trace measurements and corresponding photon statistics of the three emitters E1, E2 and E3 from in Figure 5.1 (main text) under an excitation power of 100 μW. All three emitters are stable with single-photon statistics. The higher noise level observed on the time trace of E2 is due to sample drift during measurement. .......................................................................................................... 129

Figure 5.15: PL decay time measurements of quantum emitters in GaN obtained at 4 K using a 532-nm pulsed excitation laser. a-c). Double exponential fits (red line) of the background-corrected measurements yield excited state lifetimes of 1.6, 2.7 and 2.0 ns for emitters E1, E2 and E3, respectively. ........................................................... 130

Figure 5.16: Time-resolved PL spectra of the emitters E1-E3 obtained at 4 K using an excitation power of 50μW. a-c) ZPL peak energy (left) measured every second for 2 minutes. The spectral maps show the bright yellow points as the peaks of the ZPL corresponding to the integrated spectrum (top) for each emitter. A stable mean ZPL peak energy of (1.796±0.0002) eV, (1.852±0.0005) eV and (1.981±0.0002) eV is observed for E1, E2 and E3, respectively. .............................................................. 130

Figure 6.1: Excitation power-induced blinking of an SPE in GaN. a) RT spectra of the SPE taken under 200-μW power excitation; the ZPL lies at 647 nm with an FWHM of ~4 nm. b) Fluorescence trajectory of the same emitter. The time trace is collected from the ZPL with 630 ± 30 nm bandpass filter for 2 minutes. c) Occurrence statistics of the number of photon counts in (b) over a time of 2 minutes. The emitter shows stable emission d) Fluorescence trajectory of the same emitter excited with 5 mW. The time
trace is collected from the ZPL using the same BP filter. e) Photon occurrence statistics of (d) at the same excitation power of 5 mW, with notable blinking. Time binning in (a-e) is 50 ms. f) The $g^2(\tau)$ measured for the same emitter before (red), and after (blue) the blinking was induced with high-power excitation; the $g^2(\tau)$ curves in (f) are taken with 100 $\mu$W excitation power. The blue curve is offset vertically by 1 for clarity (see Figure 6.4). The same emitter yield two different values of $g^2(0)\approx 0.24$ vs $g^2(0)\approx 0.65$ for before and after the high-power-excitation blinking was induced, respectively.

Figure 6.2: Comparison of fluorescence trajectories of the same SPE before (black) and after (red) high-power-excitation blinking was induced: [black] and [red] curves are measured at the same excitation powers. Note how at lower excitation powers (50–700 $\mu$W) the emitter shows reduced fluorescence intensity after blinking (a random blinking event is shown in the graph for 2000-$\mu$W excitation).

Figure 6.3: Sequence diagram of how the second-order autocorrelation function $g^{(2)}(0)$ and trajectory measurements were measured. First, the data is collected at low power of 0.1 mW (“before”), then the laser power is increased to induce blinking, and the same optical measurements are repeated at lower powers (“after”).

Figure 6.4: (a) RT spectra of the SPE taken under 200-$\mu$W power excitation before (red) and blue (after blinking). (b)&(c) are replots of autocorrelation curves in Figure 6.1(f) on two separate panels for better visualization of the absolute change in the antibunching dip as well as bunching curves before and after blinking.
Figure 6.5: Schematics of the transition kinetics before (a) and after (b) power-induced blinking. After blinking, a new trap state (red) is formed as shown in (b). Transition rates are indicated with $\kappa_{ij}$ where $i,j = 1,2,3,4$ indicate the ground, first electronic excited state, metastable and induced trap state, respectively. Continuous and dashed arrows indicate radiative and non-radiative transitions, respectively. 137

Figure 6.6: $g^2(0)$ measured from the SPE before and after blinking at increasing powers. Individual curves are shifted vertically for comparison purposes. For powers, 50–700 $\mu$W, the bunching effect at intermediate time scales is more pronounced in the ‘after blinking’ case than the ‘before blinking’ one. See main text. 138

Figure 6.7: Excitation-power dependent parameters of the emitter. a) The brightness of the emitter before (red) and after (blue) blinking is shown as the average photon counts at different powers. Before blinking, at saturation power ($P_{\text{sat}}$) ~660 $\mu$W, the highest intensity of 527 kcounts/s is obtained. After blinking, the saturation behaviour is fitted with a three-level model showing a remarkably different curve. b–d) Power-dependent characteristics for the fit parameters $\tau_1$, $\tau_2$, $a$, respectively, for the $g^2(\tau)$ function. These values are extracted as parameters from the $g^2(\tau)$ function fitting (Figure 6.6). A three-level model with linear power dependence for the shelving state described the transition kinetics before blinking (red fitting lines) accurately. After blinking, however, the same model fails to fit $\lambda_2$ and $a$ as highlighted by the blue lines in (c) and (d). 140
Figure 6.8: Spectroscopy and power-saturation analysis of stable and blinking emitters analysed in the study. a) Photoluminescence spectrum of the stable emitter with ZPL at 631 nm and FWHM ~8 nm. b) Saturation behaviour of the stable emitter collected using excitation power of up to 4 mW. c) Photoluminescence spectrum of an emitter that showed power induced blinking with ZPL at 652 nm and FWHM ~6 nm. d) Saturation behaviour of the blinking emitter fitted with a three-level model. The radiative transition is unaffected by the blinking behaviour.

Figure 6.9: Power-dependent long lifetime fluorescence of a stable and a blinking emitter. a) Long time scale, excitation-power-dependent $g^2(\tau)$ characteristics of a stable emitter. The best fit is determined using a single and double exponential decay function with the least chi-square value. $g^2(\tau)$ starts with monotonic decay that corresponds to ns shelving state but remains constant for the measurement time scale range of microseconds to 0.1 seconds. b) Long time scale $g^2(\tau)$ characteristics of a power-induced blinking emitter at different excitation powers. Fitting the $g^2(\tau)$ characteristics at excitation powers of 100 μW is done using single exponential decay function where $g^2(\tau)$ remained constant along the normal; whereas, for excitation power of 500–2000 μW, the emitter showed an additional bunching curve in the ms range with the height increasing with power. c) Fluorescence photostability and photon occurrence statistics under 50-ms binning for the emitter in (b) with increasing excitation power. The emitter, initially stable with near-Poissonian statistics, starts blinking for excitation powers ≥500 μW.
Figure 6.10: Probability distribution of “on” (orange) and “off” (dark yellow) states of the blinking emitter at different excitation powers. a–d) Semi-log plots of the “on” and “off” time distributions of the fluorescence trajectories shown in Figure 6.9(c). The probability distributions of both the “on” and “off” times at all excitation powers show exponential decay, as indicated by the linear trend on the semi-log plots. The “off” probability distributions hold characteristic decay time ($\tau_{\text{off}}$) that drop with increasing excitation power starting at 221.2 ms, 213.5 ms, 86.1 ms and 43.1 ms for power excitation in the range 50–2000 µW. Conversely, the “on” time distribution did not show dependence on excitation power and gave a mean characteristic decay time ($\tau_{\text{on}}$) of (548±137) ms. 

Figure 7.1: (a) Schematic illustration of a single crystal PIN diode with implanted Si-atoms and an optical image of the device. The diameters of the n-type diamond mesa are 120 µm, and the metallic contacts on top are 100 µm. (b) Monte Carlo depth profile of ion-implanted Si-atoms into diamond obtained using SRIM calculations. The end of range is estimated at 820 nm. (c) I-V-characteristic plot is showing diode rectification at a forward threshold voltage of 43V at room temperature. The inset shows Log-Linear curve of the same data set.

Figure 7.2: (a) Electroluminescence map of an 80 µm x 80 µm area showing luminescence from the edge of the pillar. (b) EL spectrum from the circled bright spot of the EL map. The EL spectrum is collected at a forward bias of 50V used to inject current of 2.9 mA into the device. (c) Photoluminescence map of a 60 µm x 60 µm area,
exhibiting comparable emission from around the edge of the pillar (d) PL spectrum from the circled bright spot of the PL map. The excitation is performed using a 532 nm cw-laser at 867 μW.

Figure 7.3: (a) Electrical driven luminescence saturation measurement of the stable SiV vacancy together with fitting curve indicated by the solid red line. (b) Shows stability measurement from the negative charge state of SiV centre when 2.5 mA of current is injected into the device. The colour centre showed stable emission for more than 6 min.

Figure 7.4: (a) Forward and reverse biased PL measurement show reduction in the intensity of the SiV⁻ ZPL. The bias voltage is varied between 52 V and -60 V. In forward bias, higher injection of carriers excites more centres resulting in higher luminescence intensity from SiV⁻ centre. As the reverse current increases, intensity from SiV⁻ decreases due to injection of holes into the centre. Charge switching to SiV⁰, however, is not observed with emission around 946 nm. (b) CL spectra from SiV ensemble at different electron beam fluence.
## Symbolic Notation

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Symbolic Notation

\begin{align*}
\boldsymbol{C}^0 & \quad \text{Neutral defect concentration} & 56 \\
\boldsymbol{C}^- & \quad \text{Ionized defect concentration} & 56 \\
\boldsymbol{C}_0 & \quad \text{Total defect concentration} & 56 \\
\boldsymbol{f} & \quad \text{Probability of occupation} & 56 \\
\boldsymbol{E}_a & \quad \text{Acceptor energy level} & 56 \\
\boldsymbol{E}_f & \quad \text{Fermi energy level} & 56 \\
\boldsymbol{C}_v & \quad \text{Concentration of point defects} & 56 \\
\boldsymbol{n}_v & \quad \text{Number of point defects} & 56 \\
\boldsymbol{N} & \quad \text{Total number of crystal electrons} & 56 \\
\boldsymbol{G}_F & \quad \text{Gibbs free energy} & 56 \\
\boldsymbol{H}_F & \quad \text{Formation enthalpy} & 56 \\
\boldsymbol{S}_F & \quad \text{Formation entropy} & 56 \\
\boldsymbol{W}_{n0} & \quad \text{Transition probability} & 56 \\
\boldsymbol{S} & \quad \text{Huang-Rhys factor} & 56 \\
\boldsymbol{E}_0 & \quad \text{Energy difference} & 57 \\
\boldsymbol{n} & \quad \text{Excitation vibrionic level} & 57 \\
\boldsymbol{a} & \quad \text{Offset parameter} & 59 \\
\boldsymbol{b} & \quad \text{Initial intensity amplitude} & 59 \\
\boldsymbol{\phi} & \quad \text{Angle between excitation laser and dipole orientation} & 59 \\
\boldsymbol{\Gamma} & \quad \text{Transform limited linewidth} & 60 \\
\boldsymbol{a}_e & \quad \text{Bohr-radius} & 70 \\
\boldsymbol{\mu}^* & \quad \text{Reduced mass} & 70 \\
\boldsymbol{m}_e & \quad \text{Mass of electron} & 70
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### List of Abbreviations

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<td>Single Photon Emitters</td>
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<td>cw</td>
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Abstract

Amanuel Michael Berhane

Spectroscopy of single photon emitting defects in Gallium Nitride and Diamond

A single photon is among the few quantum mechanical systems that are finding applications in myriad fields. The applications include serving as building blocks for the ongoing endeavour to realise faster computers and secure communication technologies. As a result, a variety of platforms are being inspected to generate single photons on-demand. Point defects and complexes in wide bandgap semiconductors such as nitrogen-vacancy (NV) and silicon-vacancy (SiV) centres in diamond, carbon antisite in Silicon Carbide (SiC), etcetera, are shown to be reliable room temperature (RT), single photon emitters (SPEs). Despite reports of several defect based SPEs in diamond and other semiconductors, the exploration continues to find ideal sources for applications. The central part of this work also focuses on the discovery and characterisation of novel SPE in the device fabrication friendly material- Gallium Nitride (GaN).

The other important aspect in the study of SPEs is the method by which emitters are excited. While optical technique via laser excitation is the standard approach, electrically excited single photon generation is highly desirable for large-scale nanophotonic applications. The second part of the work investigates electrically driven fluorescence from SiV ensemble in diamond, whose properties so far, were only investigated using optical excitations. Therefore, the thesis consists of two main parts. First, the discovery as well as study of a new family of SPEs in GaN via optical excitation is covered. The second part features electrically driven characterisation of SiV centre in diamond.
The RT stable, SPEs are discovered in GaN films using a confocal microscope. The emitters are off-resonantly excited using a continuous wave (cw) laser of wavelength 532 nm. The centre of wavelength in the emission spectra spans a wide range of from around 600 nm to 780 nm. Also, a significant portion of the emission comes from the characteristic, narrow zero-phonon lines (ZPLs) with the mean cryogenic and RT Full Width at Half Maximum (FWHM) of around 0.3 nm and 5 nm, respectively. The nature of the defect responsible for the emission is studied experimentally via temperature resolved spectroscopy as well as numerical modelling giving a strong indication that the emitter is a defect localised near cubic inclusions.

Absorption and emission polarisation properties from the SPEs in GaN is studied in detail via polarization-resolved spectroscopy. High degree of linear, emission polarisation is observed with an average visibility of more than 90 %. The absorption polarisation measurement shows that individual emitters may have different dipole orientation. In addition, brightness measurements from several of the SPEs in GaN show the average maximum intensity of around 427 kCounts/s placing the emitters among the brightest reported so far. A three-level model describes the transition kinetics of the SPEs successfully which explains some of the observed properties of the emitters such as photon statistics.

A small number of the SPEs in GaN show unusual photo-induced blinking. This blinking is shown to be due to a permanent change in the transition kinetics of the emitters when exposed to a laser power above a certain threshold. This is evidenced by the change in the transition kinetics observed before and after blinking of SPEs. Combining long-time autocorrelation measurement and photon statistics analysis, numerical values for power-dependent blinking behaviours are determined.
The second major result in this work is the first electrically driven luminescence from the negative charge state of Silicon-Vacancy (SiV\textsuperscript{−}). The result was directly obtained by measuring photoluminescence (PL) and electroluminescence (EL) spectra from SiV\textsuperscript{−} ensemble located in PIN diamond diode. The defect was incorporated into the diode via ion implantation. Further characterisation shows that the saturation behaviour under excess carrier injection yields similar results with when the defect is pumped optically by lasers. Finally, charge state switching between the negative and neutral states of the defect was also attempted by using reverse-biased PL elucidating transition dynamics of SiV centres in diamond.

This work, therefore, reports new findings in the spectroscopic studies of defect based single photon emission. Furthermore, it provides detailed photophysical studies which may serve as a benchmark for future investigation of SPEs in GaN for multiple applications. The results provide new platform as well as alternative excitation approach for the application of defect based SPEs in nanophotonics.