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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Publications

Peer-reviewed publications including one under review that contributed to this work:

1) **A. M. Berhane**, K.-Y. Jeong, Z. Bodrog, S. Fiedler, T. Schröder, N. V. Triviño, T. Palacios, A. Gali, M. Toth, D. Englund, and I. Aharonovich, "Bright Room-Temperature Single-Photon Emission from Defects in Gallium Nitride," Advanced Materials, 1605092, 29 (2017).
2) **A. M. Berhane**, C. Bradac, and I. Aharonovich, "Photoinduced blinking in a solid-state quantum system," Physical Review B **96**, 041203 (2017).
3) **A. M. Berhane**, Kwang-Yong Jeong, Carlo Bradac, Michael Walsh, Dirk Englund, Milos Toth, Igor Aharonovich, "Photophysics of Single Photon Source in Gallium Nitride at the Visible Spectrum" **(under review)**
4) **A. M. Berhane**, S. Choi, H. Kato, T. Makino, N. Mizuochi, S. Yamasaki, and I. Aharonovich, "Electrical excitation of silicon-vacancy centres in single crystal diamond," Applied Physics Letters **106**, 171102 (2015).

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

1) T. T. Tran, C. Zachreson, **A. M. Berhane**, K. Bray, R. G. Sandstrom, L. H. Li, T. Taniguchi, K. Watanabe, I. Aharonovich, and M. Toth, "Quantum Emission from Defects in Single-Crystalline Hexagonal Boron Nitride," Physical Review Applied **5** (2016). This work reports the single photon emission from bulk hexagonal Boron Nitride (hBN). Spectroscopic properties of the emission are studied using photoluminescence (PL) and cathodoluminescence (CL). The fluorescence time trace, as well as time, resolved PL is used to characterise temporal behaviours of

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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Symbolic Notation

Symbol	**Meaning**	**Page**
ω	Angular frequency	5
h	Planck’s constant	5
g^2	Second-order correlation function	13
τ	Delay time	13
I	Intensity	13
$P_{1,2}$	Probability of counting photons	15
$\eta_{1,2}$	Detection efficiency	15
Δt	Detection time	15
$\hat{n}_{1,2}$	Intensity operator	16
$\hat{a}_i$	Annihilation operator	16
$\hat{a}_i$	Creation operator	16
$\hat{a}_1$	Input field operator	17
$\hat{a}_2$	Vacuum field operator	17
n	Number of photons	17
Δn^2	Photon number variance	17
N	Number of emitters	22
p_j	Probability of emission per time	22
i_j	Discrete intensities	22
r_j	Position of emitters	22
κ_{ij}	Rate coefficients	23
λ	Eigenvalues	24

t_d	Antibunching time constant	25
q	Scaling factor	25
S	Signal counts	26
B	Background counts	26
λ_1	Radiative decay rate	28
λ_2	Non-radiative decay rate	28
a	Scaling factor for bunching	28
V_b	Potential barrier	31
E_f	Fermi energy level	32
E_e	Conduction band energy	32
E_v	Valance band energy	32
$N_{e,v}$	Intrinsic carrier concentration	32
N_d	Electron carrier density	32
N_a	Hole carrier density	32
E_g	Band gap energy	32
q	Charge of electron	32
ρ	Charge density	33
d	Width of depletion region	33
$E_{\max}$	Maximum field	34
ε	Dielectric constant	34
J_{diff}	Diffusion current	34
D	Diffusion constant	34
∇n	Concentration gradient	34
J_f	Forward current	35
J_r	Reverse current	35

V_{ext}	Applied voltage	35
ΔE	Potential step	36
K	Boltzmann constant	36
T	Temperature	36
n_i	Intrinsic concentration	37
$N_{acc(don)}$	Acceptor or donor concentration	37
τ	Lifetime	37
L	Diffusion length	37
R_d	Electron recombination rate	40
c_d	Electron capture cross-section	40
n_e	Electron density	40
f	Number of neutral defects in ground state	40
N_{SPS}	Number of single photon source per unit volume	40
c_u	Hole capture rate	41
n_p	Hole density	41
x	Population of neutral state	41
G_d	Electron generation rate	41
G_u	Hole generation rate	41
e_d	Electron re-emission rate	41
e_u	Hole re-emission rate	41
e_r	Re-emission rate of the neutral defect state	41
R_{SPS}	Recombination rate at single photon source	42
ϕ	Quantum efficiency	42
$\sigma_{d(u)}$	Capture cross-section	42
$\upsilon_{d(u)}$	Group velocity	42
P	Probability density of blinking events	45
$\tau_{On,\mathbf{Off}}$	Characteristic on- and off- blinking times	45

m_h	Mass of hole	70
ΔE_{ex}	Effective binding energy	70
κ	Semiconductor permittivity	70

List of Abbreviations

Abbreviation	Meaning	Page
SPEs	Single Photon Emitters	xxxix
GaN	Gallium Nitride	xxxix
cw	continuous Wave	xl
ZPL	Zero Phonon Line	xl
FWHM	Full Width at Half Maximum	xl
PL	Photoluminescence	xli
EL	Electroluminescence	xli
CL	Cathodoluminescence	4
PMT	Photomultiplier Tube	6
APDs	Avalanche Photo Diodes	6
HBT	Hanbury-Brown and Twiss	12
SCR	Space Charge Region	31
SPEDs	Single Photon Emitting Diodes	38
LEDs	Light Emitting Diodes	38
PD	Point Defect	55
HPHT	High-Pressure High Temperature	61
CVD	Chemical Vapor Deposition	62
SF	Stacking Fault	65
QW	Quantum Well	69
MOCVD	Metalo-Organic Chemical Vapor Deposition	74
HVPE	Hybrid Vapor Plasma Epitaxy	75
PIC	Photonic Integrated Circuit	84

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^-). The result was directly obtained by measuring photoluminescence (PL) and electroluminescence (EL) spectra from SiV^- 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.