Quantum Emission from Hexagonal Boron Nitride

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Certificate of Original Authorship

I, Trong Toan Tran, certify that the work in this dissertation entitled, “Quantum emission from Hexagonal Boron Nitride”, 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 attest that the dissertation has been written by myself. Any help that I have received in my research work and the preparation of the dissertation itself has duly been acknowledged. In addition, I certify that all information sources and literature used are indicated in the dissertation.

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To my loved ones

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List of Publications

Refereed journal publications

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2) **Tran, T. T.**; Bray, K.; Ford, M. J.; Toth, M.; Aharonovich, I. "Quantum Emission from Hexagonal Boron Nitride Monolayers." *Nat. Nanotechnol.* 2016, 11, 37-41.

3) **Tran, T. T.**; Elbadawi, C.; Totonjian, D.; Lobo, C. J.; Grosso, G.; Moon, H.; Englund, D. R.; Ford, M. J.; Aharonovich, I.; Toth, M. "Robust Multicolor Single Photon Emission from Point Defects in Hexagonal Boron Nitride." *ACS Nano* 2016, 10, 7331-7338.

4) **Tran, T. T.**; Zachreson, C.; Berhane, A. M.; Bray, K.; Sandstrom, R. G.; Li, L. H.; Taniguchi, T.; Watanabe, K.; Aharonovich, I.; Toth, M. "Quantum Emission from Defects in Single-Crystalline Hexagonal Boron Nitride." *Phys. Rev. Appl.* 2016, 5, 034005.

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Conference oral presentations

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Patents

Bishop, J.; **Tran, T. T.**; Aharonovich, I.; Lobo, C.; Toth, M. “Nanofabrication Using a New Class of Electron Beam Induced Surface Processing Techniques.” US Patent: 2017; p US20170073814 A20170073811.

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Figure 5.2. (a) *Spectra showing maximum (red trace) and minimum (blue trace) emission polarization from the emitter taken with the use of a linear polarizer. The data was taken using an excitation laser power of 300 μW with a 5 s acquisition time. The visibility was determined to be unity.* ***(b)*** *Power-dependent fluorescence saturation curve (red open circles). The fit (solid red line) produces values of* I_{max} *and* P_{sat} *of 1.3 Mcounts/sec and 1.6 mW, respectively. The measurement was acquired with a band pass filter (760 ± 12) nm. All the measurements were conducted at room temperature.*

Figure 5.3. (a) *Simplified diagram of the hBN emitter where the excited state can be accessed via either off-resonance or on-resonance excitation, with the former pathway on the left, and the latter pathway on the right. Black and grey arrows indicate excitation towards the higher vibronic states, followed by vibronic relaxation towards the excited ground state. The green arrow indicates on-*

resonance excitation, followed by spontaneous emission denoted by the wavy red arrow in both pathways. ***(b)*** *Resonance photoluminescence excitation measurements on the single emitter with a ZPL peak at 766.186 nm. The excitation power used was 150 nW. Only photons from the PSB were collected using a long pass filter. The experimental data is plotted as the red trace. Five repetitive scans were averaged out to get the final data. The data was fit with either a Gaussian function (black solid line). The measurement was done at 8 K.* ***(c)*** *Additional survey PLE scans showing multiple local maxima with FWHM below 2 GHz. The grey arrows show representative spectral features that are asymmetrical.* ***(d)*** *Time-resolved PL measurements (red open circles) of the same single emitter measured at room temperature. A single-exponential fit gives rise to a lifetime of 3.6 ns for the emitter's excited state. The measurement was done with a 675 nm pulsed laser (100 μW, 10 MHz repetition rate, 100 ps pulse width).*

Figure 5.4. *Optical characterization of another defect center.* ***(a)*** *High- and low-resolution (inset) PL spectra taken from the emitter by off-resonant excitation at 700-nm with 300μW laser power.* ***(b)*** *Five repeated scans over 60 GHz range showing some complete optical resonance features as well as some asymmetrical features.* ***(c)*** *On-resonant excitation with the laser fixed at 787.592 nm (red solid line) and 2-nm detuned from the on-resonance excitation wavelength (black solid line). The calculated* $\tau_{ON}/\tau_{OFF} = 0.09$ *indicates that the emitter is mostly in unexcited states.*

Figure 5.5. (a) *PL intensity vs time for on-resonance (red line) and 2 nm detuned (black) excitation of the same emitter. The blue dash line represents the cut-off threshold (1800 count/sec) for calculating* τ_{on} *and* τ_{off}*. The* τ_{on} / τ_{off} *ratio was calculated to be 0.47. The data are vertically shifted for clarity.* ***(b)*** *Histogram of on-resonance time extracted from an on-resonance trace of* ***(a)****. The calculated average spectral diffusion time,* $\tau_{avg\ spec\ diff} = 102 \pm 65$ *ms.* ***(c)*** *Confocal PL map with the laser staying on-resonance (left panel) and 2 nm detuned (right panel)*

from the resonance. The measurements in ***(a)*** *and* ***(b)*** *were carried out at the excitation power of 150 nW.* ***(d)*** *On-resonance photon second-order correlation function (black open circles) acquired for the emitter at 1 μW excitation power for three hours. The red solid line is the fitting for the* $g^{(2)}_{meas}(0)$ *function using the Gaussian-convoluted three-level model, resulting in an antibunching dip value of 0.11 ± 0.04. The standard deviation was based on the standard deviation taken from the long delay time region. It must be noted that no smoothing procedure was implemented for this measurement. All the measurements were conducted at 8 K.*

Figure 6.1. (a) *Optical image of exfoliated hBN flakes.* ***(b)*** *Table of the investigated samples comprised of a reference sample, four samples that were implanted by ions, one processed by a laser beam and one by an electron beam.*

Figure 6.2. (a-d) *PL spectra from hBN flakes implanted with B, BN, O and Si ions. The insets are second-order autocorrelation functions,* $g^{(2)}(\tau)$*, recorded from each sample, demonstrating the emitters are single photon sources. A spectrum from a reference sample and a corresponding* $g^{(2)}(\tau)$ *function are shown in the (****Fig. 6.8****).*

Figure 6.3. (a) *A table comparing the number of formed emitters found in each ion-implanted sample and a reference sample that was only subjected to annealing.* ***(b, c)*** *Examples of stability curves from a single emitter in an ion implanted flake* ***(b)*** *and in a reference flake* ***(c)****. Blinking followed by bleaching was much more common in the reference sample than in the implanted samples.*

Figure 6.4. *Confocal maps from* ***(a-c)*** *B,* ***(d-f)*** *BN,* ***(g-i)*** *O and* ***(j-l)*** *Si implanted hBN flakes, demonstrating unambiguously that the emitters are always localized at flake edges. Large bright features seen away from flake edges, as in map* ***(i)****, do not exhibit photon antibunching, and do not possess the spectral characteristics of the single photon emitters discussed in this study.*

Figure 6.5. (a-d) *Example of excitation (red circles) and emission (blue squares) polarization plots of single emitters* from each of the implanted samples. All the emitters exhibit dipole like behavior in both excitation and emission.

Figure 6.6. *Fabrication of emitters using laser processing.* ***(a)*** *Confocal map of the hBN flakes. The white circle indicates the presence of the location of a single photon emitter.* ***(b)*** *PL spectrum recorded from the emitter. Inset:* $g^{(2)}(\tau)$ *curve confirming it is indeed a single photon emitter.* ***(c)*** *excitation and emission polarization curves (red circles and blue squares, respectively,) recorded from this emitter.*

Figure 6.7. *Fabrication of emitters by electron beam irradiation. Confocal map of the same flake before* ***(a)*** *and after* ***(b)*** *electron beam irradiation. The energy of the beam is 15 keV.* ***(c)*** *Spectra recorded from a particular location before (blue curve) and after (red curve) irradiation. Inset, a* $g^{(2)}(\tau)$ *curve confirming the formed defect is a single photon source.* ***(d)*** *Excitation and emission polarization from the same defect. The sample was not annealed after electron irradiation.*

Figure 7.1. *Hexagonal boron nitride flakes and their transfer process onto plasmonic lattice substrates.* ***(a)*** *Schematic illustration of the wet process used to transfer a selected hBN flake with an emitter of choice (exemplified by the red dot) from a thermal silicon oxide substrate onto a plasmonic NP array using PMMA as the carrier.* ***(b)*** *SEM image of the mechanically exfoliated hBN flake positioned atop of a silver plasmonic lattice on silica and* ***(c)*** *optical image of the same flake on the plasmonic lattice.* ***(d)*** *FDTD simulation of the lateral (in-plane) electric field intensity distribution* $|E|^2$ *of a 400 nm-spacing silver plasmonic lattice structure.*

Figure 7.2. *Finite-difference time-domain simulation of the vertical (cross-sectional) electric field intensity distribution* $|E|$ *of a silver nanoparticle (NP) array with 400-nm spacing.*

Figure 7.3. *Confocal PL map* ***(a)*** *and its corresponding larger field-of-view SEM image* ***(b)*** *shown in main text* ***Fig. 6.2a****. A good spatial correlation between the confocal map and the SEM image can be observed. The SEM image unarguably shows that the flakes are positioned atop the gold plasmonic NP array.*

Figure 7.4. *Coupling between a quantum emitter in a tape exfoliated hBN flake and a gold NP array on silica.* ***(a)*** *PL confocal map of a flake containing a single photon emitter (red circled). Inset, SEM image of part of the flake on top of the gold plasmonic lattice. The scale bar represents 2 μm.* ***(b)*** *PL spectra of the pristine (red trace) and coupled (blue trace) single photon emitter, and a transmission spectrum of the plasmonic lattice (green trace) with the plasmonic resonance at 640 nm.* ***(c)*** *Second-order autocorrelation functions obtained from the pristine (red circles) and coupled (blue open squares) system. In both cases, the dip at zero delay time falling well below 0.5 implies single photon emission. Background correction was employed to correct the antibunching curves due to high PL background coming from the hBN flake. The* $g^{(2)}(0)$ *values for emission from pristine and coupled emitters are at 0.02 and 0.04, respectively. Red and blue solid lines are fits obtained using a three-level model.* ***(d)*** *Time-resolved PL measurements from the pristine (red open circles) and coupled (blue open squares) systems. Red and blue solid lines are double exponential fits. A 532 nm continuous-wave laser was used in* ***(a)****,* ***(b)*** *and* ***(c)****. A 512 nm pulsed laser with a repetition rate of 10 MHz and 100 ps pulse width was used in* ***(d)****.*

Figure 7.5. *A full-range transmission spectrum of a gold array in Fig. 7.4. The solid line implies the 532 nm excitation laser used in this study. There is a negligible pump absorption by the plasmonic array according to the spectrum.*

Figure 7.6. *Confocal PL maps of before and after the solvent-exfoliated flakes being transferred onto the plasmonic NP array. The two maps show a good agreement on the spatial location and relative orientation of the flakes to one another, confirming that the same flakes were examined.*

Figure 7.7. *Coupling between a quantum emitter in a solvent exfoliated hBN flake and a gold NP array on a silica substrate.* ***(a)*** *PL spectra of a pristine (red trace) and coupled (blue trace) single photon emitter, and a transmission spectrum of the gold lattice (green trace). Inset: SEM image of the hBN flakes ontop the gold NP array.* ***(b)*** *Second-order autocorrelation functions obtained from the pristine (red open circles) and coupled (blue open squares) systems. The* $g^{(2)}(0)$ *values for emission from pristine and coupled emitters are 0.23 and 0.47, respectively. In both cases, the dip at zero delay time falling well below 0.5 implies single photon emission. Red and blue solid lines are fits obtained using a three-level model.* ***(c)*** *Time-resolved PL measurements from the pristine (red open circles) and coupled (blue open squares) systems. Red and blue solid lines are double exponential fits.* ***(d)*** *Fluorescence saturation curves obtained from the pristine (red open circles) and coupled (blue open squares) systems. Red and blue solid lines are fits obtained using equation 2. A 532 nm continuous-wave laser was used in* ***(a)****,* ***(b)*** *and* ***(d)****. A 512 nm pulsed laser with a repetition rate of 10 MHz and 100 ps pulse width was used in* ***(c)****.*

Figure 7.8. *Coupling between a quantum emitter in a solvent exfoliated hBN flake and a silver NP array on a silica substrate.* ***(a)*** *PL spectra of a pristine (red trace) and coupled (blue trace) single photon emitter, and a transmission spectrum of the silver lattice (green trace).* ***(b)*** *Second-order autocorrelation functions obtained from the pristine (red open circles) and coupled (blue open squares) systems. In both cases, the dip at zero delay time falling well below 0.5 implies single photon emission. Red and blue solid lines are fits obtained using a three-level model. The* $g^{(2)}(0)$ *values for emission from pristine and coupled emitters are 0.06 and 0.29, respectively.* ***(c)*** *Time-resolved PL measurements from the pristine (red open circles) and coupled (blue open squares) systems. Red and blue solid lines are double exponential fits.* ***(d)*** *Fluorescence saturation curves for obtained from the pristine (red open circles) and coupled (blue open squares) systems. Red and blue*

solid lines are fits obtained using equation 2. A 532 nm continuous-wave laser was used in ***(a)****,* ***(b)*** *and* ***(d)****. A 512 nm pulsed laser with a repetition rate of 10 MHz and 100 ps pulse width was used in* ***(c)****.*

Figure 8.1. *Characterization of the multilayers.* ***(a)*** *Optical image of annealed WS_2 multilayers. The scale bar is 10 μm. No visible difference could be seen before and after annealing.* ***(b)*** *Raman spectra of a pristine monolayer (red), pristine multilayer (green), and multilayers that were annealed in argon at 550°C (blue). The grey and yellow highlighted boxes denote E_{2g} and 2LA mode, and A_{1g} vibration mode of WS_2.* ***(c)*** *TEM image of an annealed flake and* ***(d)*** *the corresponding selected area electron diffraction taken from* ***(c)****. The diffraction pattern indicates the cubic phase of WO_3.* ***(e-g)*** *XPS spectra of WS_2 annealed at 550°C in an Argon atmosphere, showing spectral regions that contain the O_{1s}, S_{2p} and W_{4f} peaks, respectively. In* ***(c)*** *the presence of a WO_x phase is clearly observed.*

Figure 8.2. *Bright-field optical images of WS_2 flakes after being annealed at 550°C in argon for 30 min. The scale bars are 10 μm. The WS_2 flakes have lateral size of ~0.3 – 3 μm and thickness of ~5 – 300 nm.*

Figure 8.3. *Single photon emission from annealed multilayers.* ***(a)*** *A typical confocal photoluminescence map showing several bright spots corresponding to localized defects.* ***(b)*** *Photoluminescence spectra taken from three bright spots. A spectrum from monolayer WS_2 is plotted for comparison* ***(c)*** *Second-order autocorrelation measurement obtained from the three emitters. The curves are offset vertically for clarity.* ***(d)*** *Time-resolved photoluminescence measurement recorded from the three emitters, yielding excited state lifetimes of 3.5 ns, 4.6 ns, and 4.4 ns, respectively for emitters S1, S2 and S3. The pump power used in* ***(a, b, c)*** *was 300 μW at 532 nm while the pulsed measurement was done using a 512 nm laser (10 MHz, 50 μW).*

Figure 8.4. *Fluorescence saturation and polarization of emitter S1.* ***(a)*** *Fluorescence intensity as a function of pump power. The red open circles and grey open triangles denote background-corrected fluorescence profile of emitter S1 and background fluorescence taken at an area adjacent to the emitter (in* ***Fig. 8.3****). The solid lines are corresponding fitted curves. The saturated intensity is 347,000 cps with the saturated pump at 1.9 mW.* ***(b)*** *Excitation (red open circles) and emission (blue open squares) measurement for emitter S1. Solid lines are corresponding fits.* ***(c)*** *Fluorescence stability measurement over 10 minutes at an excitation power of 1mW. No bleaching or blinking could be seen from the measurement. Measurements taken in* ***(a-c)*** *were done with CW 532 nm laser.*

Figure 8.5. *Additional polarization data taken from three different single photon emitters from the annealed WS_2 sample. Red open circles and blue open squares denote excitation and emission measurement, respectively. Solid lines are corresponding fits. Measurements were done with CW 532 nm laser.*

Figure 8.6. (a) *Antibunching curves as a function of pump power. Solid lines are fitted profile using the standard three-level model.* ***(b)*** *Emission (τ_1) and metastable (τ_2) lifetime plotted as a function of excitation power. By applying linear fitting and extrapolating the fits to vanishing excitation power, emission (τ_1) and metastable (τ_2) lifetime are calculated to be 4.5 ns and 9.3 ns, respectively.* ***(c)*** *Proposed three-level diagram of the emitters with a ground state, an excited state, and a metastable state. Black, red and grey arrows represent excitation, emission, and non-radiative transitions.*

List of Tables

Abbreviations

0D – zero dimensional

1D – one dimensional

2D – two dimensional

3D – three dimensional

APD – avalanche photodiode

CL – cathodoluminescence

CVD – chemical vapor deposition

CW – continuous wavelength

EPR – electron paramagnetic resonance

FIB – focused ion beam

FWHM – full width at half maximum

hBN – hexagonal boron nitride

HBT – Hanbury Brown and Twiss

IRF – instrument response function

NIR – near infra-red

PL – photoluminescence

PSB – phonon sideband

ODMR – optically detected magnetic resonance

QDs – quantum dots

QE – quantum efficiency

QIP – quantum information processing

QKD – quantum key distribution

SEM – scanning electron microscope

SPS – single photon source

SRIM – stopping and range of ions in matter

WS_2 – tungsten disulfide

ZPL – zero phonon line

Abstract

Realization of quantum technologies demands successful assembly of crucial building blocks. Quantum light sources, lying at the heart of this architecture, have attracted a great deal of research focus during the last several decades. Optically active defect-based centers in wide bandgap materials such as diamond and silicon carbide have been proven to be excellent candidates due to their high brightness and photostability. Integration of quantum emitters on an on-chip integrated circuit, however, favors low dimensionality of the host materials. Single photon sources embedded in two-dimensional lattices are, therefore, highly desired. In this thesis, we introduce a class of novel quantum systems hosted in hexagonal boron nitride (hBN) – a wide bandgap semiconductor in the two-dimensional (2D) limit. First, we demonstrate experimentally that the quantum systems possess a record high single photon count rate, exceeding 4 MHz at room temperature. Polarization and time-resolved spectroscopy reveal their full emission polarization and short excited state lifetime (~3 ns). Besides, the emitters from this class of quantum system also show extremely high stability under high excitation at ambient conditions. By employing spin-resolved density functional theory (DFT) calculation, we suggest that the defect center is an antisite nitrogen vacancy (N_BV_N). A multicolor phenomenon where there is a wide distribution of zero-phonon lines (ZPL) from different emitters is also observed and can be attributed to strain field in the hBN lattice thanks to DFT calculation. Additionally, we demonstrate the ability to create the emitters by means of thermal treatment or electron beam induced etching. Under harsh environments, strikingly, most of the emitters survive and preserve their quantum properties. Resonant excitation spectroscopy reveals a linewidth of ~6 GHz, and a high single photon purity confirmed from an emitter by on-resonance antibunching measurements. Studies on bulk hBN crystals reveal that the emitters tend to locate at dislocations or stacking faults in the crystals. We also demonstrate ion implantation and laser

ablation as means of increasing formation yield of the emitters in mechanically exfoliated hBN flakes. Next, the coupling of quantum emitters in hBN to plasmonic particles arrays is demonstrated, showing several times Purcell enhancement factor. Lastly, we show that another 2D material - tungsten disulfide (WS_2) – when being oxidized also hosts quantum emitters at room temperature. This observation, therefore, opens a new avenue for studying quantum emitters embedded in other 2D materials.