

DOCTORAL THESIS

**Quantum Emitters for Sensing and
Sub-Diffraction Imaging**

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for the degree of Doctor of Philosophy

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Certificate of Original Authorship

I, Mehran KIANINIA, certify that the work in this thesis titled, ‘Quantum Emitters for Sensing and Sub-Diffraction Imaging ’ 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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Contributing Publications

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- Robust Solid-State Quantum System Operating at 800 K, **M. Kianinia**, B. Regan, S. A. Tawfik, T. T. Tran, M. J. Ford, I. Aharonovich, M. Toth. In: *ACS Photonics*, 4.4 (2017), pp. 768–773.
- Super-resolution imaging of quantum emitters in layered materials, **M. Kianinia**, C. Bradac, B. Sontheimer, F. Wang, T. T. Tran, M. Nguyen, S. Kim, Z. Xu, D. Jin, A. W. Schell, C. Lobo, I. Aharonovich, M. Toth. In: *Nature Communications*, (2018).
- Attachment of nano-objects to beam-deposited structures, **M. Kianinia**, Olga Shimoni, Igor Aharonovich, Charlene Lobo, Milos Toth, Steven Randolph, Clive D Chandler. U.S. Patent Application 15/188862, (2017).

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- Resonant excitation of quantum emitters in hexagonal boron nitride, Toan Trong Tran, **Mehran Kianinia**, Minh Nguyen, Sejeong Kim, Zai-Quan Xu, Alexander Kubanek, Milos Toth and Igor Aharonovich. In: *ACS Photonics*, (2017).

- Single Photon Emission from Plasma Treated 2D Hexagonal Boron Nitride, Zai-Quan Xu, Christopher Elbadawi, Toan Trong Tran, **Mehran Kianinia**, Timothy B Hoffman, Minh Nguyen, Sejeong Kim, James H Edgar, Ziaojun Wu, Li Song, Sajid Ali, Mike Ford, Milos Toth and Igor Aharonovich. In: *Arxiv*, (2017), arXiv:1710.07010.
- Optical properties of implanted Xe color centers in diamond, Russel Sandstrom, Li ke, Aiden Martin, Ziyu Wang, **Mehran Kianinia**, Ben Green, Weibo Gao and Igor Aharonovich. In: *Optics Communications*, 411 (2018), pp.182-186.
- Nanoassembly of quantum emitters in hexagonal boron nitride and gold nanospheres, Minh Nguyen, Sejeong Kim, Toan Trong Tran, Zai-Quan Xu, **Mehran Kianinia**, Milos Toth, and Igor Aharonovich. In: *Nanoscale*, 10 (2018), pp. 2267-2274.
- Nanodiamonds with photostable, sub-gigahertz linewidths quantum emitters, Toan Trong Tran, **Mehran Kianinia**, Kerem Bray, Sejeong Kim, Zai-Quan Xu, Angus Gentle , Bernd Sontheimer, Carlo Bradac and Igor Aharonovich. In: *APL Photonics*, 2 (2017), pp 116103-116112.

Conference presentations

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Abstract

A quantum system with discrete, resolvable energy levels is an ideal system for sensing applications, taking into account that it can strongly interact with its environment. Although the strong response with the target properties such as magnetic or electric field is ideal, it can be a disadvantage when the system is interacting with other physical changes (noise) at the same time. However, the benefits of the strong coupling as well as small size of the sensor has motivated many researchers to explore quantum systems for measuring very small physical quantities. For instance, Nitrogen vacancy center in diamond is a unique quantum system enabling sensing of magnetic field from single molecules or electrons at room temperature.

This thesis has focused on two different quantum emitters: NV centers in nanodiamonds and quantum emitters in hexagonal Boron Nitride (hBN). In the first part a new assembly technique based on electron beam induced deposition and crosslinking chemistry is developed. It is demonstrated that fluorescent nanodiamonds containing NV centers can be assembled into arrays of various size and shapes on any substrate. The produced array is ideal for device fabrication due to its outstanding robustness. A potential application of such arrays as magnetic field sensor with high spatial resolution is shown.

The superior properties of quantum emitters in hBN has been studied in the second part of this thesis, where it has been shown that these emitters are not only stable but also maintain their single photon purity at elevated temperature. The highest measured quantum emission at 800 K in this study is the highest reported temperature for a quantum emitter so far, makes them a suitable candidate for temperature sensing. In addition, the level structure of emitters in hBN has been investigated in detail which reveals the unique photophysical properties of a class of these emitters which result in a nonlinear increase in the emission upon co-excitation with two lasers of different wavelength. Finally the photophysical property of these emitters has been employed to introduce a new modality of super-resolution microscopy with resolution down to about 70 nm. These findings will extend our understanding of

quantum emitters in hBN and introduce a new functionality for them which paves the way toward their application in biology and sensing.

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Abbreviations

AFM	Atomic Force Microscope
BSE	Backscattered Electron
QD	Quantum Dot
SQUID	Superconducting Quantum Interference Device
LED	Light Emitting Diode
CVD	Chemical Vapour Deposition
ODMR	Optically Detection Magnetic Resonance
SE	Secondary Electrons
EBID	Electron Beam Induced Deposition
EBIE	Electron Beam Induced Etching
OES	Optical Emission Spectroscopy
RIE	Reactive Ion Etching
ESEM	Environmental Scanning Electron Microscope
MFC	Mass Flow Controller
FCC	Fluorescence Cross Correlation
RESOLFT	Reversible Saturable Optical Linear Fluorescence Transitions
CW	Continuous Wave
ISC	Inter System Crossing
PSF	Point Spread Function
RF	Radio Frequency
NMR	Nuclear Magnetic Resonance
NV	Nitrogen-Vacancy

NV ⁰	Neutral Nitrogen-Vacancy
NV ⁻	Negative Nitrogen-Vacancy
PL	Photoluminescence
MW	MicroWave
NA	Numerical Aperture
SCCM	Standard Cubic Centimeters per Minute
STED	Stimulated Emission Depletion
GSD	Ground State Depletion
ZPL	Zero Phonon Line
SPS	Single Photon Source
DFT	Density Functional Theory
EDC	1-ethyl-3-(3-dimethylaminopropyl)carbodiimide hydrochloride
NHS	N-hydroxysuccinimide
FWHM	Full Width Half Maximum
TMP	Turbo Molecular Pump
CNT	Carbon NanoTube
RT	Room Temperature
APD	Avalanche Photo-diode
HBT	Hanbury Brown and Twiss
TCSPC	Time Correlated Single Photon Counting