UNIVERSITY OF TECHNOLOGY SYDNEY

DOCTORAL THESIS

Electron beam processing and spectroscopic characterisation of 2D materials and novel nanostructures

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Declaration of Authorship

I, Christopher ELBADAWI, declare that this thesis titled, "Electron beam processing and spectroscopic characterisation of 2D materials and novel nanostructures" and the work presented in it are my own. I confirm that:

- This work was done while in candidature for a research degree at this University.
- Where any part of this thesis has previously been submitted for a degree or any other qualification at this University or any other institution, this has been clearly stated.
- Where I have consulted the published work of others, this is always clearly attributed.
- Where I have quoted from the work of others, the source is always given. With the exception of such quotations, this thesis is entirely my own work.
- I have acknowledged all main sources of help.
- Where the thesis is based on work done by myself jointly with others, I have made clear exactly what was done by others and what I have contributed myself.
- This research is supported by an Australian Government Research Training Program Scholarship.

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Abstract

Interest in the inorganic two-dimensional (2D) materials black phosphorus (BP) and hexagonal boron nitride (hBN) has exponentially risen due to the distinct advantages they possess over their bulk counterparts. Excellent and unique mechanical, electronic and optical properties have recently been discovered which can potentially span a large range of conceptually new applications such as high speed flexible electronics, sub-diffractional nanophotonic devices, strain engineered variable sensors and robust quantum information processing systems.

To take advantage of these unique properties a greater understanding of the underlying chemical mechanisms involved in the manipulation/modification of BP and hBN is required. In this project, the nanofabrication tool focused electron beam induced processing (FEBIP) is used to do this all within a scanning electron microscope (SEM). FEBIP is a nanofabrication technique in which electrons are used to decompose surface adsorbed precursor molecules, typically under a constant partial pressure of a precursor gas. A highly focused beam can be used to deposit or etch nanoscale structures on a solid substrate. This technique differentiates itself from classical growth methods through other unique aspects, which include; growth of fully realised three-dimensional (3D) nanostructures, selective surface termination, defect generation and real-time imaging of chemical reaction fronts.

The aim of this project was to elucidate experimentally the fundamental processes that govern the chemical reactions occurring during FEBIP. The first study outlined in this thesis involves the creation of an automated scanning program to reliably manipulate the electron beam for accurate data acquisition and pattern formation. To showcase these capabilities, 3D Pt nanostructures such as high aspect ratio pillars and helices fabricated with $Pt(PF_3)_4$-mediated electron beam induced deposition. Post-growth annealing in a water vapour environment was found to improve Pt deposit

purity by volatilising phosphorus contaminants in the form of phosphoric acid. Annealing in H_2O under optimized conditions, yielded platinum that is pure within the detection limit of wavelength dispersive x-ray spectroscopy.

Following from the information obtained through purification of phosphorus contaminants, attention was focused on the simulation of degradation of the highly unstable few-layer BP via electron beam irradiation performed *in-situ*. The real time imaging capabilities allowed for rapid stabilisation techniques to be found via controlled gas mixing and temperature dependent studies. The degradation pathway was found to proceed through the creation of phosphoric acid in a H_2O environment and is shown to be dependent on temperature. A low temperature heat cycle was then formulated to remove intercalated water and oxygen species to cease the degradation of few-layer BP for up to four weeks per heat cycle.

Next, chemical dry etching of hexagonal Boron Nitride (hBN) was performed in a water vapour environment to create nanostructure geometries such as high resolution patterns, nanoribbons, and particles with high fidelity. Steps are also taken toward deterministic generation of defects and single photon emitters in hBN. The product of the electron induced dissociation of hBN at the surface of the material results in the production of nitrogen and boron radicals which then react with H_2O to produce boric and nitric acids. These then can be used as etch precursors for other materials such as silver nanowires. This two step etching process was then reimagined using an *in-situ* delocalised plasma and electron beam irradiation to widen the scope of etch-able materials such as silver, using a gas phase etch process.

These results broaden the scope of material selection available in FEBIP. The exploitation of the unique aspects demonstrated with this technique in this project increases the applicability and versatility of FEBIP as a prominent tool for nanofabrication of 2D materials and complex 3D nanostructures. Furthermore, the results presented here constitute' the first step towards integration of few-layer BP and hBN into high-performance optoelectronic devices, quantum information systems and various environmental sensor applications.

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Publications

Peer-reviewed publications list:

- Pure Platinum Nanostructures Grown by Electron Beam Induced Deposition. **C. Elbadawi**, M. Toth, and C. Lobo. ACS applied materials and interfaces (2013), 5(19), 9372-9376.

- Electron beam directed etching of hexagonal boron nitride. **C. Elbadawi**, T. T. Trang, J. Scott, M. Kolibal, T. Šikola, Q. Cai, L. Li, T. Taniguchi, K Watanabe, M. Toth, I. Aharonovich and C. Lobo. Nanoscale (2016), 16182-16186.

- Ambient stabilization of few-layered black phosphorus by thermal cycling. **C. Elbadawi**, R. Tormo Queralt, X. Zaiquan, J. Bishop, T. Ahmed, S. Kuriakose, S. Walia, M. Toth, I. Aharonovich and C. Lobo. Submitted.

- Robust multicolor single photon emission from point defects in hexagonal boron nitride. T. T. Trang, **C. Elbadawi**, C. Lobo, D. Totonjian, G. Grosso, H. Moon, I. Aharonovich, and M. Toth. ACS Nano (2016), 7331-7338.

- Ambient protection of few-layer black phosphorus via sequestration of reactive oxygen species. S. Walia, S. Balendhran, T. Ahmed, M. Singh, **C. Elbadawi**, M.D. Brennan, P. Weerathunge, M. Karim, F. Rahman, A. Rassell, J. Duckworth, A. Ramanathan, G.E. Collis, C.J. Lobo, M. Toth, J.C Kotsakidis, B. Weber, F. Michael, J.M. Dominguez-Vera, M.J.S. Spencer, I. Aharonovich, S. Sriram, M. Bhaskaran and V. Bansal. Advanced materials (2017) May 12.

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- Engineering and localization of quantum emitters in large hexagonal boron nitride layers. S. Choi, T. T. Trang, **C. Elbadawi**, C. Lobo, W. Xuewen, S. Juodkazis, G. Seniutinas, M. Toth, and I. Aharonovich. ACS applied materials and interfaces (2016), 29642-29648.

- Growth of Three Dimensional Nanostructures by Electron Beam Induced Deposition. J. Bishop, **C. Elbadawi**, M. Kianinia, J. Pritchard, C. Lobo, and M. Toth. Submitted.

- Micro-Patterned Surfaces that Exploit Stigmergy to Inhibit Biofilm Expansion. E. Gloag, **C. Elbadawi**, C. Zachreson, I. Aharonovich, M. Toth, I. Charles, L. Turnbull and C. Whitchurch. Frontiers in Microbiology (2017), 7 (2016): 2157.

- Single Photon Emission from Plasma Treated 2D Hexagonal Boron Nitride. Z. Xu, **C. Elbadawi**, T. T. Trang, M. Kianinia, X. Li, D. Liu, T. B. Hoffman, M. Nguyen, S. Kim, J. H. Edgar, X. Wu, L. Song, S. Ali, M. Ford, M. Toth and I. Aharonovich. Submitted.

- Deterministic Nanopatterning of Diamond Using Electron Beams. J. Bishop, M. Fronzi, **C. Elbadawi**, V. Nikam, J. Pritchard, M. Ford, I. Aharonovich, C. J. Lobo and M. Toth. ACS Nano (2017), 10.1021/acsnano.8b00354 24 Jan 2018.

- Ultra-bright emission from hexagonal boron nitride defects as a new platform for bio-imaging and bio-labelling. **C. Elbadawi**, T. T. Trang, O. Shimoni, D. Totonjian, C. J. Lobo, G. Grosso, H. Moon, D.R. Englund, M.J. Ford, I. Aharonovich and M. Toth. SPIE BioPhotonics Australasia. Vol. 10013. International Society for Optics and Photonics, 2016.

Conference Presentations

Conference presentation list:

- Nanotechnology Workshop for Early Career Researchers, Flinders University, July 2013. Oral presentation: Localized fabrication of pure platinum nanostructures – Awarded best presentation

- FEBIP 2016, TU Wien Austria, Vienna July 2016. Oral presentation: Electron beam restructuring of hexagonal Boron Nitride for applications in photonics and polaritonics

- SPIE BioPhotonics Australasia, Adelaide October 2016. Oral presentation: "Ultra-bright emission from hexagonal boron nitride defects as a new platform for bio-imaging and bio-labelling." SPIE BioPhotonics Australasia. Vol. 10013. International Society for Optics and Photonics, 2016.

- COMMAD 2016, UNSW, Sydney 2016 Oral Presentation: Electron beam driven defect creation in hexagonal Boron Nitride for photonic applications

- 253rd American Chemical Society National Meeting and Expo, San Francisco 2017 Oral presentation: Directed deposition and etching using electron beam and plasma irradiation

List of Figures

List of Abbreviations

2D	Two-Dimensional
AFM	Atomic Force Microscope
BP	Black Phosphorus
BSE	Backscattered Electron
CASINO	Monte Carlo Simulation of Electron Trajectory in Solids
CCD	Charge-Coupled Device
CNT	Carbon Nanotubes
CVD	Chemical Vapour Deposition
DFT	Density Functional Theory
EBID	Electron Beam Induced Deposition
EBIE	Electron Beam Induced Etching
EBL	Electron Beam Lithography
EDS	Energy-Dispersive X-ray Spectroscopy
ESEM	Environmental Scanning Electron Microscope
FEBIP	Focused Electron Beam Induced Processing
FLBP	Few Layer Black Phosphorus
FEG	Field Emission Gun
FIB	Focused Ion Beam
FWHM	Full Width at Half-maximum
GIS	Gas Injection System
hBN	Hexagonal Boron Nitride
HBT	Hanbury Brown and Twiss
MoS_2	Molybdenum Disulfide
MoO_3	Molybdenum trioxide

NIDAQ	National Instruments Data Acquisition Device
RF	Radio Frequency
RIE	Reactive Ion Etching
ROS	Reactive Oxygen Species
PSB	Phonon Side Band
PL	Photoluminescence
SAED	Selected Area Electron Diffraction
SEM	Scanning Electron Microscope
SDD	Silicon Drift Detector
SPE	Single Photon Emitter
TMD	Transition Metal Dichalcogenides
TEM	Transmission Electron Microscope
WDS	Wavelength-Dispersive X-ray Spectroscopy
ZPL	Zero Phonon Line

List of Symbols

FEBIP model

Adsorption

N_d	Concentration of precursor adsorbates (molecules/Å^2)
s_d	Precursor adsorbate sticking coefficient
J_d	Precursor molecular flux (Å$^2 s^{-1}$)
p	Gas pressure (Pa)
m	Molecular mass of the precursor (g)
A_d	Precursor molecule surface area (Å^2)
t	Time (s)

Desorption

E_d	Energy barrier for desorption (J/molecule)
v_0	Vibrational frequency of the adsorbed molecule (Hz)

Diffusion

r	Radial distance from electron beam axis (Å)
D	Diffusion coefficient (Å^2 s^{-1})
E_{diff}	Energy barrier for diffusion (J/molecule)
T	Temperature (K)
k_b	Boltzmann constant (J/K)
D_0	Diffusion prefactor (Å^2 s^{-1})

Dissociation

N_D	Number of deposited molecules per unit area (molecules/Å^2)
f	Electron flux (e/Å^2/s)
σ_d	Adsorbate dissociation cross-section (Å^2)
V_D	Volume of the deposited material (Å^3)

Interaction volume

A	Atomic weight (g/mol)
EL	Landing energy (keV)
p	Density (g/cm^3)
Z	Atomic number

Typical Experimental parameters used
for studies completed in this thesis

ESEM conditions	
Beam current	0.1 - 8 nA
Accelerating voltages	1 - 30 keV
gas pressures	8 - 20 Pa
Plasma Conditions	
Frequency	131 MHz
Power	5 W
PL conditions	
Laser frequencies	533 nm, 632 nm
Power	300 μW
Raman Conditions	
Laser frequencies	633 nm

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