

UNIVERSITY OF TECHNOLOGY SYDNEY

DOCTORAL THESIS

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

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*in the*

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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:

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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-diffractive 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  $\text{Pt}(\text{PF}_3)_4$ -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<sub>2</sub>O 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<sub>2</sub>O 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<sub>2</sub>O 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 reimaged 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. Russell, 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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- 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*

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- 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



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# List of Abbreviations

<b>2D</b>	Two-Dimensional
<b>AFM</b>	Atomic Force Microscope
<b>BP</b>	Black Phosphorus
<b>BSE</b>	Backscattered Electron
<b>CASINO</b>	Monte Carlo Simulation of Electron Trajectory in Solids
<b>CCD</b>	Charge-Coupled Device
<b>CNT</b>	Carbon Nanotubes
<b>CVD</b>	Chemical Vapour Deposition
<b>DFT</b>	Density Functional Theory
<b>EBID</b>	Electron Beam Induced Deposition
<b>EBIE</b>	Electron Beam Induced Etching
<b>EBL</b>	Electron Beam Lithography
<b>EDS</b>	Energy-Dispersive X-ray Spectroscopy
<b>ESEM</b>	Environmental Scanning Electron Microscope
<b>FEBIP</b>	Focused Electron Beam Induced Processing
<b>FLBP</b>	Few Layer Black Phosphorus
<b>FEG</b>	Field Emission Gun
<b>FIB</b>	Focused Ion Beam
<b>FWHM</b>	Full Width at Half-maximum
<b>GIS</b>	Gas Injection System
<b>hBN</b>	Hexagonal Boron Nitride
<b>HBT</b>	Hanbury Brown and Twiss
<b>MoS<sub>2</sub></b>	Molybdenum Disulfide
<b>MoO<sub>3</sub></b>	Molybdenum trioxide

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



# List of Symbols

## FEBIP model

### Adsorption

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

### Desorption

$E_d$	Energy barrier for desorption (J/molecule)
$\nu_0$	Vibrational frequency of the adsorbed molecule (Hz)

### Diffusion

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

## Dissociation

$N_D$	Number of deposited molecules per unit area (molecules/ $\text{\AA}^2$ )
$f$	Electron flux ( $e/\text{\AA}^2/\text{s}$ )
$\sigma_d$	Adsorbate dissociation cross-section ( $\text{\AA}^2$ )
$V_D$	Volume of the deposited material ( $\text{\AA}^3$ )

## Interaction volume

$A$	Atomic weight (g/mol)
$EL$	Landing energy (keV)
$p$	Density ( $\text{g}/\text{cm}^3$ )
$Z$	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  $\mu W$

Raman Conditions

Laser frequencies 633 nm



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