Doctoral Thesis

Gas-Mediated Electron Beam Induced Etching

A thesis submitted in fulfilment of the requirements
for the degree of Doctor of Philosophy

School of Physics and Advanced Materials
University of Technology, Sydney

Author
Aiden Alexander Martin

Supervisors
Prof. Milos Toth
Dr. Charlene Lobo
Prof. Matthew Phillips
A. Prof. Igor Aharonovich

June 2015

Certificate of Original Authorship

I, Aiden Alexander Martin, certify that the work in this thesis titled, 'Gas-Mediated Electron Beam Induced Etching' 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.

Signature of Student: Production Note: Signature removed prior to publication.

Date: 12 June 2015

Acknowledgements

I would like to express my deepest thanks to Professor Milos Toth. I am sincerely grateful for the opportunities you have provided during this work and for the future. I would also like to thank Dr. Charlene Lobo, Professor Matthew Phillips and Associate Professor Igor Aharonovich. All of you have given me exceptional guidance and made my time at UTS a truly enjoyable experience.

My sincere thanks to Associate Professor Mike Ford, Mr. Geoff McCredie, Mrs. Katie McBean, Dr. Angus Gentle and Mr. Mark Berkahn for your support over the last decade of work and study.

To my fellow students, I would like to thank all of you for your friendship. A special thank you to James Bishop, Toby Shanley, Cameron Zachreson, Alan Bahm and Russell Sandstrom for allowing me to collaborate with you on your research projects. James Bishop assisted with the electron beam induced etching of diamond experiments featured in Chapter 4.

Thank you Dr. Eric Silver, Dr. Ting Lin, Mr. Gerry Austin and Mr. David Caldwell at the Harvard-Smithsonian Center for Astrophysics for your generosity and stimulating discussions during our collaboration. Eric Silver and Ting Lin performed the energy-dispersive x-ray spectroscopy measurements and hosted the equipment used for the experiments featured in Chapter 8.

I would like to thank FEI Company for their financial and scientific support. The training provided by your organisation has allowed me to travel the world and work with amazing people. Steven Randolph and Aurelien Botman of FEI Company irradiated a diamond sample with oxygen ions for the study in Chapter 6. Thank you to the Science and Industry Endowment Fund for the John Stocker Postgraduate Scholarship, which has enabled collaborations with international researchers. I would also like to thank the Australian Nanotechnology Network and Microscopy Society of America for their conference travel funding.

A special thanks to my family for always nurturing my creativity and preparing me for all of lifes challenges. Lastly and most of all I would like to thank my wife Amanda. Your support, encouragement and love made this work possible.

Contributing Publications

Peer-reviewed publications that contributed to this work:

- Dynamic surface site activation: A rate limiting process in electron beam induced etching, **A. A. Martin**, M. R. Phillips and M. Toth, ACS Appl. Mater. Interfaces, 5 (16), p. 8002 – 8007, 2013
- Subtractive 3D printing of optically active diamond structures, **A. A. Martin**, M. Toth and I. Aharonovich, Sci. Rep., 4, 5022, 2014
- Cryogenic electron beam induced chemical etching, **A. A. Martin** and M. Toth, ACS Appl. Mater. Interfaces, 6 (21), p. 18457 – 18460, 2014
- Maskless milling of diamond by a focused oxygen ion beam, **A. A. Martin**, S. Randolph, A. Botman, M. Toth and I. Aharonovich, Sci. Rep., 5, 8958, 2015, 2015

Non-Contributing Publications

Peer-reviewed publications not featured in this work containing research undertaken during the PhD program:

- Electron beam induced chemical dry etching and imaging in gaseous NH_3 environments, C. J. Lobo, **A. Martin**, M. R. Phillips and M. Toth, Nanotechnology, 23 (37), p. 375302, 2012. This work demonstrated NH_3-mediated electron beam induced etching (EBIE) of carbonaceous material. Etching is highly material selective, and does not volatilise ultra nano-crystalline diamond to any significant degree. The process is also effective at preventing the buildup of residual hydrocarbon impurities that often compromise EBIE, electron beam induced deposition (EBID) and electron imaging.

- Role of activated chemisorption in gas-mediated electron beam induced deposition, J. Bishop, C. J. Lobo, **A. A. Martin**, M. Ford, M. R. Phillips and M. Toth, Phys. Rev. Lett., 109 (14), p. 146103, 2012. This work investigated the rate kinetics of EBID using tetraethoxysilane (TEOS) precursor. Chemisorbed states govern the adsorbate coverage and EBID rates at elevated substrate temperatures. The results show how EBID can be used to deposit high purity materials and characterise the rates and energy barriers that govern precursor adsorption.

- Localized chemical switching of the charge state of nitrogen-vacancy luminescence centers in diamond, T. Shanley, **A. A. Martin**, I. Aharonovich and M. Toth, Appl. Phys. Lett., 105 (6), p. 063103, 2014. This work demonstrated electron beam induced functionalisation of diamond. Fluorination of H-terminated diamond is realised by electron beam stimulated desorption of surface adsorbed H_2O in the presence of NF_3.

- Electron beam-controlled modification of luminescent centers in a polycrystalline diamond thin film, C. Zachreson, **A. A. Martin**, M. Toth and I. Aharonovich, ACS Appl. Mater. Interfaces, 6 (13), p. 10367 - 10372, 2014. This work investigated room temperature activation of several luminescence centres in diamond through a thermal mechanism that is catalysed by an electron beam. Cathodoluminescence activation kinetics were measured in real-time and attributed to electron induced dehydrogenation of nitrogen-vacancy-hydrogen clusters and dislocation defects.

- Study of narrowband single photon emitters in polycrystalline diamond films, R. G. Sandstrom, Olga Shimoni, **A. A. Martin** and I. Aharonovich, Appl. Phys. Lett., 105 (18), p. 181104, 2014. This work investigated the photophysical properties of bright, narrowband single photon emitters in diamond films grown on a silicon substrate by microwave plasma chemical vapor deposition.

Contents

List of Figures

List of Tables

Abbreviations

AFM	Atomic Force Microscope
BSE	Backscattered Electron
CASINO	Monte Carlo Simulation of Electron Trajectory in Solids
CCD	Charge-Coupled Device
CL	Cathodoluminescence
CVD	Chemical Vapour Deposition
DEA	Dissociative Electron Attachment
DEI	Dissociative Electron Ionisation
EBID	Electron Beam Induced Deposition
EBIE	Electron Beam Induced Etching
EDS	Energy-dispersive X-ray Spectroscopy
eCell	Environmental Reaction Cell
ESEM	Environmental Scanning Electron Microscope
FIB	Focused Ion Beam
HFCVD	Hot Filament Chemical Vapour Deposition
ICPS	Inductively Coupled Plasma Source
LN	Liquid Nitrogen
NASA	National Aeronautics and Space Administration
PLA	Pressure Limiting Aperture
RF	Radio Frequency
RRL	Reaction-rate Limited
NV	Nitrogen-Vacancy
NV^0	Neutral Nitrogen-Vacancy

NV^-	Negative Nitrogen-Vacancy
PL	Photoluminescence
PPM	Parts per Million
SEM	Scanning Electron Microscope
SCCM	Standard Cubic Centimetres per Minute
UNCD	Ultra Nano-crystalline Diamond
XANES	X-ray Absorption Near Edge Structure
ZPL	Zero Phonon Line

Abstract

Gas-mediated electron beam induced etching is a direct-write nanolithography technique. In this thesis, through experimental observation and numerical simulation, descriptions of reaction kinetics of electron beam induced etching were refined to include effects of residual contaminants, substrate material properties, and temperature dependence. Reaction kinetics of electron beam induced etching are of interest because they affect resolution, throughput, proximity effects, and topography of nanostructures and nanostructured devices fabricated by electron beam induced etching.

A number of mechanisms proposed in the literature for electron beam induced removal of carbon were shown to be insignificant. These include atomic displacements caused by knock-on by low energy electrons, electron beam heating, sputtering by ionised gas molecules, and chemical etching driven by a number of gases that include N_2. The behaviour ascribed to these mechanisms was instead explained by chemical etching caused by electron beam induced dissociation of residual contaminants such as H_2O present in the vacuum systems that are typically used for EBIE.

Reaction mechanisms in single crystal and ultra nano-crystalline diamond were shown to be dependent on substrate material properties. Single crystal diamond etch morphology is attributed to anisotropic etching along crystal planes, which varies with precursor composition. In contrast to single crystal diamond, etching of ultra nano-crystalline diamond was shown to proceed via an electron activated pathway. A refined electron beam induced etching model incorporating the role of electron induced damage in ultra nano-crystalline diamond yields higher order reaction kinetics, predicting a new reaction regime limited by the concentration of chemically active surface sites.

A temperature dependent, cryogenic electron beam induced etching technique was implemented to increase the residence time of adsorbates on the surface. This technique efficiently increases the rate of electron beam induced etching, demonstrated using nitrogen trifluoride as the etch precursor for silicon. Cryogenic cooling broadens the range of precursors that can be used for electron beam induced etching, and enables high-resolution,

deterministic etching of materials that are volatilised spontaneously by conventional etch precursors.

Determining the reaction kinetics of electron beam induced etching enables new applications in nanoscale material modification. Methods for the fabrication of optically active, functional diamond structures from single crystal diamond and rapid Stardust particle extraction were demonstrated. Electron beam induced etching is ideal for these applications, where high-resolution, damage-free etching is required.