

DOCTORAL THESIS

**Predictive modelling of gas assisted electron and ion beam
induced etching and deposition**

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

Alan Stephen BAHM

Supervisors

Prof. Milos TOTH

Associate Prof. Michael FORD

July 2016

Certificate of Original Authorship

I, Alan Stephen BAHM, certify that the work in this thesis titled, 'Predictive modelling of gas assisted electron and ion beam induced etching and deposition' 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:

Date: 28 July 2016

Acknowledgements

The work presented in this dissertation was carried out under the supervision of Prof. Milos Toth and Prof. Michael Ford, at the Microstructural Unit, Faculty of Science, University of Technology Sydney, New South Wales, Australia. The work was performed within the Advanced Technology Group, Beam Technology R&D, FEI Company, Hillsboro, Oregon, U.S.A.

I am extremely grateful to FEI Company for making this work possible through its financial and scientific support. Dr. Michael Lysaght supported this work through the ups and downs of business cycles. Dr. Mark Utlaut and Dr. Mostafa Maazouz envisioned the collaboration. Greg Schwind's support and flexibility helped greatly. Dr. Lynwood Swanson was an inspiring mentor who demonstrated how to approach rigorous research. Dr. Mostafa Maazouz first engaged me in simulation of FIB surface evolution by allowing me to build on the research by Dr. Heung-Bae Kim on the level set method. I benefited from many useful discussions over the years with Dr. Mark Utlaut, Dr. Marcus Straw, Dr. Mostafa Maazouz and Dr. William Parker.

At the University of Technology Sydney (UTS), many people also made this research possible. I'm especially appreciative for my advisor, Prof. Milos Toth, who was key throughout the definition and focussing of the work, and also challenged me to improve. Prof. Michael Ford advised, acted as a sounding board and provided feedback. Collaborations and interactions with Prof. Charlene Lobo and Prof. Igor Aharonovich always improved the work at hand.

I would like to thank many remote collaborators including Dr. Branislav Radjenovic, Prof. David Chopp, Prof. Ian Mitchell and Prof. Colin Macdonald for emails and discussions on etch interpolation models, level set method and closest point methods. Additionally valuable were discussions with Dr. Sloan Lindsey, Prof. Gerhard Hobler on ion-solid interactions as well as general discussions with Dr. Utlaut, Dr. Maazouz, Greg Schwind and Prof.dr.ir. Peter Kruit. I had a wonderful group of scientists and students to work with at FEI and UTS: my thanks to my co-authors Dr. Aurelian Botman, Dr. Steven Randolph, Dr. Aiden Martin, Dr. Marcus Straw, Dr. Chad Rue, Dr. Jared Cullen, Chris Badawi, Toby Shanley, and James Bishop.

I was truly lucky to have support from my family and friends. My wife 潘恒彦 (Heng-Yen Pan) and son William Bahm gracefully supported me through the upheaval in our family life over the last three and a half years. My parents and sister were loving and wonderfully supportive, as was

our adoptive family Joel Godbey, Kelly Morrow, Eric Miller and Missy Yungclas. Finally, a big thank you to Keith Wilson who gave me lab space in which to work, feedback and companionship.

Contributing Publications

Peer-reviewed publications that contributed to this work:

- Spontaneous Growth of Gallium-Filled Microcapillaries on Ion-Bombarded GaN, Aurelien Botman, **Alan Bahm**, Steven Randolph, Marcus Straw, and Milos Toth *Physical Review Letters* 111, 135503 - Published 25 September 2013
- Dynamic Pattern Formation in Electron-Beam-Induced Etching, Aiden A. Martin, **Alan Bahm**, James Bishop, Igor Aharonovich, and Milos Toth *Physical Review Letters* 115, 255501 - Published 18 December 2015

Non-Contributing Publications

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

- Localized Probing of Gas Molecule Adsorption Energies and Desorption Attempt Frequencies, Jared Cullen, **Alan Bahm**, Charlene J. Lobo, Michael J. Ford, and Milos Toth, *Journal of Physical Chemistry C*, 2015, 119 (28), pp 15948-15953

Contents

Certificate of Original Authorship	ii
Acknowledgements	iii
Contributing Publications	v
Non-Contributing Publications	vi
List of Figures	xi
List of Tables	xiii
Abbreviations	xv
Physical Constants	xvii
Symbols	xix
Abstract	xxi
1 Motivation and background	1
1.1 What is EBIED / IBIED?	1
1.2 Modelling of EBIED / IBIED with a gas precursor	2
1.3 Experimental EBIED / IBIED	3
1.4 Outline of thesis	4
2 Gallium fluoride pillar modelling	5
2.1 Spontaneous growth of gallium-filled microcapillaries on ion-bombarded GaN	6
2.2 Model implementation	15
2.2.1 Model results	17
2.3 Self-ordering cycle	19
2.4 Conclusions	22
3 Surface evolution modelling	23
3.1 Dynamic pattern formation in electron beam induced etching	24
3.2 Level set method	30
3.2.1 Concept	32

3.2.2	Reinitialization	35
3.2.3	Non-convex Hamiltonian	35
3.2.4	Discretization and choice of scheme	35
3.2.5	Sparse field	37
3.2.6	Fast marching method	37
3.2.7	Extension velocity	38
3.3	Implementation and verification	38
3.4	Diamond etch model implementation	40
3.4.1	Etch rate anisotropy	40
3.4.2	Simulation verification	41
3.4.3	Determination of anisotropic etch rates	43
3.5	Conclusions	44
4	Adsorbate kinetics modelling	45
4.1	EBIED / IBIED PDE definition	46
4.2	Techniques for solving PDEs on surfaces	47
4.2.1	Explicit surface techniques	47
4.2.2	Implicit surface techniques	47
4.2.3	The closest point method technique	48
4.2.4	Other applications of CPM	48
4.2.5	Recent developments with CPM	48
4.3	Closest point method	49
4.4	Implementation and verification of CPM	51
4.4.1	Implementation of diffusion	54
4.4.2	Implementation of sources and sinks	54
4.5	Simulating adsorbate deposition	56
4.5.1	Steady state assumption	57
4.5.2	Deriving closest points on implicit surface from ϕ	57
4.5.3	Ghost widths	58
4.5.4	Results	61
4.6	Conclusions	63
5	General conclusions and future directions	65
5.1	Including sample interactions	65
5.2	Conclusions	67
A	Ion solid interactions modelling	69
A.1	Overview	70
A.2	Ion solid collision theory	71
A.2.1	Total stopping	71
A.2.2	Electronic stopping	72
A.2.3	Nuclear stopping	75
A.2.4	Classical scattering event	75

A.2.4.1	Derivation of kinetic energy as a function of scattering angle	76
A.2.4.2	Derivation of scattering integral	79
A.2.4.3	Screened coulomb potential	80
A.2.4.4	Implications of mass mismatch	80
A.3	Binary collision algorithm	81
A.3.1	Biersack's "scattering triangle"	83
A.3.2	Implementation	85
A.3.3	Validation and Results	86
A.3.3.1	Flat surfaces	88
A.3.3.2	Curved surfaces	89
A.4	Conclusions	90
B	Framework for EBIED / IBIED adsorbate continuum equations	93
B.1	Species i	94
B.2	Species concentration N	94
B.3	Flux of electrons, ions, and neutrals	96
B.4	Transport \mathcal{T}	98
B.5	Addition \mathcal{A}	100
B.5.1	Adsorption	100
B.5.2	Thermal dissociation	101
B.5.3	Stimulated dissociation	102
B.5.4	Fragment combination	103
B.5.5	Thermal chemisorption	103
B.5.6	Stimulated chemisorption	103
B.5.7	Redeposition of sputtered material	104
B.5.8	Volume evolution	104
B.5.9	Total addition	104
B.6	Removal \mathcal{R}	104
B.6.1	Thermal desorption	105
B.6.2	Stimulated desorption	105
B.6.3	Associative desorption	105
B.6.4	Fragment combination	106
B.6.5	Thermal dissociation	106
B.6.6	Stimulated dissociation	106
B.6.7	Thermal etching	106
B.6.8	Stimulated etching	107
B.6.9	Thermal chemisorption	107
B.6.10	Stimulated chemisorption	107
B.6.11	Sputtering	107
B.6.12	Consumption in surface reactions	107
B.6.13	Total removal	108
B.7	Conclusions	108
C	Modelling code	109

D Arrhenius form	111
Bibliography	113

List of Figures

1.1	EBIED and IBIED surface schematic	1
2.1	Ga droplets and GaF pillars	8
2.2	Growth of a pillar	9
2.3	Evolution of pillar geometry and material distribution	10
2.4	Cross-sectional compositional maps	11
2.5	Coalescence of pillar caps	11
2.6	Gallium concentration on substrate	14
2.7	Numerical implementation of the model	16
2.8	Sheath volume calculation	18
2.9	Example model output	20
2.10	Self-ordering cycle schematic	21
3.1	Pattern formation by H ₂ O on diamond	26
3.2	Pattern formation by NH ₃ on diamond	28
3.3	Temperature dependence of EBIE rate	29
3.4	Level set image segmentation	31
3.5	Level set method publications	31
3.6	Illustration of level set in two dimensions	33
3.7	Non-convex Hamiltonian from sputter yield	36
3.8	Level set implementation verification convex scheme	39
3.9	Level set implementation verification non-convex scheme	40
3.10	Etch rate regions	41
3.11	Etching of spheres and voids	42
3.12	Diamond etching scheme	44
4.1	Illustration of locally oriented basis on surface	50
4.2	Role of Cartesian points in the closest point method	51
4.3	Illustration of closest point operator on local grid	52
4.4	Illustration of L and G bands	53
4.5	Sparse matrices of the closest point method	54
4.6	Stabilization of M matrix	55
4.7	Demonstration of heat diffusion	56
4.8	Demonstration of adsorbate diffusion	57
4.9	Demonstration of adsorbate diffusion	58
4.10	Illustration of CPM-LSM improvement by reinitialization domain	59

4.11	Illustration of ghost width for CPM initialization from ϕ	60
4.12	Illustration of mass transfer limited surface evolution 2D	62
4.13	Illustration of mass transfer limited surface evolution 3D	64
5.1	Computing sample interaction, adsorbate kinetics and surface evolution	66
A.1	Ion solid interactions	71
A.2	Nuclear, electronic and total stopping cross sections	72
A.3	Silicon stopping cross sections	73
A.4	Silicon stopping cross section models	74
A.5	Scattering event	76
A.6	Lab and centre of mass reference frames	78
A.7	Screened potentials	81
A.8	Implications of mass mismatch	82
A.9	Definition of scattering triangle	85
A.10	Comparison of scattering approaches	86
A.11	Example trajectories in 3D	87
A.12	Sputter yield agreement	88
A.13	Example cascades	89
A.14	Sputter yields on hemicylinders	90
A.15	Sputter yields on hemispheres	91
B.1	Map of surface processes	95
B.2	Elemental surface interactions	99
B.3	Elemental surface interactions (continued)	100
B.4	Reaction-coordinate diagram across potential barrier	102
D.1	Boltzmann distributions	111

List of Tables

2.1	Sheath volume calculation	19
3.1	Simulation etch rates	43
C.1	Simulation code statistics	110

Abbreviations

API	Application Programming Interface
BCA	Binary Collision Algorithm
BET	Brunauer-Emmett-Teller theory
BDF	Backwards Difference Formula
CM	Centre of Mass
CPM	Closest Point Method
CPU	Central Processing Unit
EBIE	Electron Beam Induced Etching
EBIED	Electron Beam Induced Etching and Deposition
EDS	Energy Dispersive X-ray Spectroscopy
FEM	Finite Element Methods
FMM	Fast Marching Method
FVM	Finite Volume Methods
GIS	Gas Injection System
GPU	Graphics Processing Unit
FIB	Focused Ion Beam
HJE	Hamilton-Jacobi Equation
iSE	Ion Generated Secondary Electrons
ISM	Ion-Solid-Modelling
ITK	Insight Segmentation and registration Toolkit
IBIED	Ion Beam Induced Etching and Deposition
LLF	Local-Lax-Friedrichs
LF	Lax-Friedrichs

LSM	Level Set Method
MC	Monte Carlo
MD	Molecular Dynamics
MTL	Mass Transport Limited
PDE	Partial Differential Equation
RD	Reaction Diffusion
SEM	Scanning Electron Microscope
SIMD	Single Instruction Multiple Data
SRIM	Stopping and Range of Ions in Matter (software program)
TEM	Transmission Electron Microscope
TRIM	Transport and Range of Ions in Matter (software program)
TRIDYN	Transport of Ions (Dynamic)
UV	Ultraviolet
1D	One Dimensional
2D	Two Dimensional
3D	Three Dimensional

Physical Constants

Bohr radius	a_0	=	$5.291\,772\,109\dots \times 10^{-11}$	m
Electron rest mass	m_e	=	$9.109\,382\,15\dots \times 10^{-31}$	kg
Vacuum permittivity	ϵ_0	=	$8.854\,187\,817\dots \times 10^{-12}$	F/m
Pi	π	=	3.14159...	
Euler's number	e	=	2.71828...	

Symbols

R^3	real coordinate space of three dimensions
∇	gradient
∇^2 or Δ	Laplacian a.k.a. Laplace operator
∇_S	intrinsic gradient
∇_S^2 or Δ_S	intrinsic Laplacian a.k.a. Laplace-Beltrami operator
Δ	discrete difference
∂x	partial derivative of x
dx	total derivative of x
$t \rightarrow 0$	“as t goes to zero”
$\mathbf{x}, \mathbf{v}, \mathbf{n}, \mathbf{t}$	vector position, velocity, normal, tangent
κ	curvature
ϕ_t	time derivative of ϕ
\hat{H}	exact Hamiltonian
H	discretized approximation of the Hamiltonian
max	maximum
$O(N)$	big O notation
$F_{ext}(\phi = 0) = F$	“extension velocity at $\phi = 0$ is F”
log	logarithm base 10
ln	natural logarithm
\approx	approximately equal to
\equiv	definition
cos, tan, cot	cosine, tangent, cotangent function
$cp()$	closest point operator

Abstract

While the field of experimental micrometre scale EBIED / IBIED (“electron beam chemistry” or “ion beam chemistry”) has been growing in recent years, the 3D simulation of these systems at real scales has been non-existent. This type of simulation is important for it is only in three dimensions that interesting asymmetric and patterning phenomena can be tracked.

There are a couple of difficulties in these types of simulations. One is solving the diffusion of adsorbate concentrations in the system. Accurate simulation of diffusion on general 2D surfaces is non-trivial, (even on 1D curves), and can require unnatural re-parametrization of the surface (re-meshing). Another difficulty is that simulations have generally been atomistic and limited in scale. The key to providing large scale 3D simulations comes from applying new, mathematically robust, computer-science methods based on implicit surfaces to this field.

In this thesis, the issues above are addressed in a couple of different ways. In one case, diffusion over a complex surface was reduced to piecewise axially symmetric equations. Later, implicit methods for solving adsorbate kinetics continuum equations and evolving the surface are implemented, the closest point method and the level set method respectively. The development of the tools themselves is a non-trivial exercise as there are few software libraries for the level set method and none for the closest point method. These tools were then used independently to simulate etching and diffusion, as well as in concert to demonstrate the ability to simulate 3D deposition in the mass transport limited and reaction rate limited regimes.

