### UNIVERSITY OF TECHNOLOGY, SYDNEY

DOCTORAL THESIS

## Localised Probing of Precursor Coefficients Using Electron Beam Induced Deposition and Etching

Author: Jared Craig Cullen Supervisor: A Prof. Mike FORD, Prof. Milos TOTH, & Dr. Charlene LOBO

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

 $in \ the$ 

Materials and Technology for Energy Efficiency School of Physics and Advanced Materials

January 2016

## **Declaration of Authorship**

I, Jared Craig CULLEN, declare that this thesis titled, Localised Probing of Precursor Coefficients Using Electron Beam Induced Deposition and Etching, and the work presented in it is my own.

- I certify that the work in this thesis 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.

Signed:

Date:

#### UNIVERSITY OF TECHNOLOGY, SYDNEY

### Abstract

Faculty of Science School of Physics and Advanced Materials

Doctor of Philosophy

### Localised Probing of Precursor Coefficients Using Electron Beam Induced Deposition and Etching

by Jared Craig CULLEN

Electron beam induced etching (EBIE) and deposition (EBID) are direct-write deposition techniques in which an electron beam is used for chemical precursor dissociation. Both techniques are capable of nanometer-scale resolution, but applications have been limited by poor understanding of the underlying reaction mechanisms and rate parameters. Here, a hybrid Continuum-Monte Carlo model has been designed and implemented, enabling modelling of the temporal and spatial evolution of nanostructures fabricated by EBID and EBIE. This hybrid model is used to perform Arrhenius analysis of the deposition rates of nanostructures grown by EBID and EBIE, from which both precursor desorption and diffusion rate parameters can be obtained. These parameters are of fundamental interest in physical chemistry and surface science fields but also are key to optimisation of chemical vapour deposition (CVD), EBID, EBIE, and related surface processing and nanofabrication techniques. Methods used to determine the activation energy and pre-factors for desorption and diffusion are described in detail. The limitations of these methods, growth conditions needed to minimise errors, and applications to the chemistry, physics and nanotechnology communities are also discussed.

## A cknowledgements

My PhD has been an eventful ride full of ups and downs, but throughout it all a number of people have helped me persevere and I would like to take the time now to thank them.

My supervisors, A Prof. Michael J. Ford, Prof. Milos Toth, and Dr. Charlene Lobo, thank you all for the support you gave me across the many years, it has been invaluable. Whether it be coming up with solutions to software bugs or bouncing around ideas for papers I could always count on all of you. Also, a special thank you to Mr. Alan Bahm for introducing me to a number of new programming concepts and just always being an email away when I needed help.

My uni mates, Mark Lockrey, Chris Elbadawi, Kit Fair, James Bishop, thanks guys for helping me in the lab and the many problems I had...talking it out really helps; I'll really miss the dumpling lunches.

My university, University of Technology, Sydney, thank you to everyone who has taught me across the many the years and for giving me a place to study in several courses for the 9+ years that I've been there.

My family, Mum, Dad, and my brother, thank you for always being there when I needed to talk about something and giving me advice or even reminding me to call when I haven't in a while...I hope I've made you proud.

My partner, Juainni, thank you most of all for sticking by me all these years, especially when it seemed to go on and on. You have no idea how much that means to me.

To the many people that I've most likely forgotten, thank you too.

-Jared

## Contents

D	eclar	ation o	of Authorship	ii
$\mathbf{A}$	Abstract Acknowledgements			
A				
$\mathbf{Li}$	st of	Figure	es	viii
$\mathbf{Li}$	st of	Tables	5	xiii
1	Intr	oducti	ion	1
	1.1	Projec	t Objectives and Approach	. 1
	1.2	Thesis	Outline	. 2
	1.3	Publis	hed Work	. 3
<b>2</b>	Lite	erature		<b>4</b>
	2.1	Physic	al Processes	. 5
		2.1.1	Adsorption	. 5
		2.1.2	Desorption	. 6
		2.1.3	Surface Diffusion	. 7
		2.1.4	Electron Induced Dissociation	. 7
	2.2	Exper	imental Applications	. 8
		2.2.1	The Effect of Various Experimental Parameters	. 9
		2.2.2	Resolution of EBID structures	. 11
	2.3	Model	ling Methods	. 13
		2.3.1	Continuum Models	. 13
		2.3.2	Monte Carlo Models	. 17
	2.4	Summ	ary	. 21
3	Hył	orid Co	ontinuum-Monte Carlo Model	<b>22</b>
	3.1	Contir	num Equations	. 25
		3.1.1	Discretization of Time and Space	. 27
		3.1.2	Verification	. 30
	3.2	Electro	on Trajectory Simulation	. 33
		3.2.1	Single Scattering Model	. 35
		3.2.2	Parametric Model	. 39

		3.2.3 Model Extensions
		3.2.3.1 Backscattered & Forward Scattered Electrons 40
		$3.2.3.2  \text{Secondary Electrons}  \dots  \dots  \dots  \dots  \dots  \dots  \dots  \dots  \dots  $
		3.2.4 Verification
	3.3	Model Extensions
		3.3.1 Surface Evolution & Electron Beam Projection
		3.3.2 Surface Diffusion Modelling
		$3.3.2.1$ Free Form Movement $\ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots 50$
		$3.3.2.2  \text{Area Remapping}  \dots  \dots  \dots  \dots  \dots  \dots  \dots  \dots  \dots  $
		3.3.3 Verification
<b>4</b>	Hyl	rid Model Simulator Details 55
	4.1	User Operation
	4.2	Tutorial: How to run the EBIED simulator
		4.2.1 Mac OS X
		4.2.2 Ubuntu - Linux
	4.3	Summary of Parameters within the EBIED Simulator Input File 62
		4.3.1 Simulation Parameters
		4.3.2 Electron Beam Parameters
		4.3.3 Material Parameters
		4.3.4 Precursor Parameters
		4.3.5 Module Toggles
		4.3.6 Miscellaneous Parameters
	4.4	Summary of Outputs from the EBIED Simulator
	4.5	Summary of Warning and Error Messages within the EBIED Simulator 70
<b>5</b>	Loc	lized Probing of Gas Molecule Adsorption Energies and Desorption
	Att	mpt Frequencies 74
	5.1	Introduction
	5.2	Arrhenius analysis of deposition rates
		5.2.1 Athermal adsorption flux condition
		5.2.2 Reaction-rate limited growth condition
		5.2.3 Negligible diffusion condition $\ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots $
		5.2.4 Steady state growth condition $\ldots \ldots $
	5.3	General implications for the determination of adsorbate properties 80
	5.4	Conclusion
6	Elec	tron Beam Induced Deposition As a Technique for the Analysis of
	$\mathbf{Pre}$	Sursor Molecule Diffusion Barriers and Pre-Factors 89
	6.1	Introduction
	6.2	Roles of Desorption and Diffusion in EBID
	6.3	Adsorbate Transport Through Diffusion
	6.4	Extraction of Diffusion Energies and Pre-Exponential Factors 94
	6.5	Pre-requisites

	6.6	6.5.2 6.5.3 6.5.4 Limita	Condition 2 - Significant adsorbate concentration gradient Condition 3 - Diffusion-dominated replenishment	. 99 . 100 . 101 . 103
	6.7	Conclu	191011	. 104
7	Con	clusio	n	106
$\mathbf{A}$	Diff	usion '	Test Code	107
в	Hyb	orid Co	ontinuum-Monte Carlo Simulator Code	112
	B.1	Consta	ants	. 112
	B.2	Variab	ble Structures	. 112
	B.3	Functi	on Prototypes	. 114
	B.4	Simula	ator Core	. 119
	B.5	EBID/	/EBIE & EBIED Solver	. 142
	B.6	Electro	on Flux Profile	. 153
	B.7	Linear	Interpolation	. 157
	B.8	Monte	Carlo Data Collection	. 158
	B.9	Monte	Carlo Electron Trajectories	. 162
	B.10	Monte	Carlo Surface Setup	. 182
	B.11	Read 1	Input Parameters	. 184
	B.12	Read 1	Previous Simulation Data	. 194
	B.13	Outpu	t Current Simulation Data	. 195
	B.14	Create	e Output Files	. 199
	B.15	Crank	-Nicholson Solver	. 200
	B.16	Surfac	e Evolution	. 201
	B.17	Print	to Logfile	. 206
$\mathbf{C}$	Mod	del De	rivations	208
	C.1	EBID/	/EBIE - Uniform Grid Spacing Derivation	. 208
		C.1.1	Von Neumann Stability	. 211
	C.2	EBID/	/EBIE - Non-Uniform Grid Spacing Derivation	. 216
	C.3	EBIEI	D - Derivation	. 219
		C.3.1	Deposit Precursor Gas Concentration	. 219
		C.3.2	Etchant Precursor Gas Concentration	. 221
		C.3.3	Deposited Molecule Concentration	. 223
Bi	bliog	graphy		<b>224</b>

# List of Figures

2.1	(Figure Replicated from Hoffmann, et al.[13]) The key concepts of EBIED	
	technique: adsorption, desorption, surface diffusion, and electron beam in-	
	duced dissociation of precursor molecules. The particular precursor deter-	
	mines whether the resultant dissociation product causes deposition or etching.	4
2.2	(Figure Replicated from Li, et al.[16]) Schematic diagram of the potential	
	energy as a function of the distance from the surface	5
2.3	The electron cross section of gaseous $H_2O$ at various electron energies [24].	8
2.4	(Figure Replicated from Schoenaker et al.[50]) (a) Dependence of the etching	
	depth on the etching time for several beam currents. (b) Etching rate and	
	yield for different beam currents. The experiment was performed by using	
	a beam energy of 2 kV. The rate and yield calculations do not take into	
	account the peripheral etching	11
2.5	(Figure Replicated from Choi et al.[62]) (a) Deposition of tungsten pillar	
	under different biased conditions. (b) Scattering of electron (SE, BSE, and	
	PE) on the tungsten pillar under different biases	12
2.6	(Figure Replicated from Lobo, et al. [69]) (a) Growth rate plotted as a	
	function of radius (r) from the beam axis, calculated using currents of 0.4,	
	0.5, 0.52, 0.53, 0.55, 0.6, 0.7, 0.8 and 1 nA. Also shown is the total electron	
	flux profile from figure 1(d). (b) Surface plots of the 0.4, 0.5 and 0.6 nA	
	deposition rate profiles (linear scale) ( $P_d = 10^{-2}$ Pa)	15
2.7	(Figure Replicated from Bishop et al.[63]) Steady state adsorbate dissocia-	
	tion rates calculated using Eqs. $(4)$ - $(6)$ as a function of substrate tempera-	
	ture, and the corresponding deposition rates measured using tetraethoxysi-	
	lane precursor ( $\circ$ )	16
2.8	(Figure Replicated from Silvis-Cividjian et al. [76]) A typical curve showing	
	the evolution of the cone diameter	18
2.9	(Figure Replicated from Smith et al.[74]) Normalized comparison of the	
	MTL pillar shape, RRL pillar shape, and Gaussian beam profiles. These	
	profiles were taken from the I keV MTL and RRL pillars at the same height	
	(12.5 nm). 100 000 random Gaussian samples of a 3 nm diameter beam	10
0.10	superimposed on the substrate surface to snow the beam profile.	19
2.10	(Figure Replicated from Smith et al.[75]) Cross sections through the top 50	
	nin of the pillars at varying diffusion coefficients. Top row, left to right: $1.0 \times 10^{-8}$ $1.0 \times 10^{-9}$ and $1.0 \times 10^{-10}$ $2^{-1}$ . Better row left to right:	
	$1.0 \times 10^{\circ}$ , $1.0 \times 10^{\circ}$ , and $1.0 \times 10^{-5}$ cm <sup>2</sup> s <sup>-1</sup> . Bottom row, left to right:	90
	$1.0 \times 10^{\circ}$ , and $0.0 \text{ cm}^{-}\text{s}^{-}$	20

3.1	(Figure Replicated from Utke, et al. [4]) AFM image and line scans of FEB deposits from $Cu(hfac)_2$ precursor. Exposure times are indicated. Indented apex shapes are due to depletion. Dashed lines represent gaussian fits of each deposit.	23
3.2	(Figure Adapted from Smith, et al. [74] with a CASINO Monte Carlo sim- ulation of electron trajectories overlayed.) 2D time-resolved cross-sectional profiles and deposition events (based on electron type) from the gas dynam- ics simulations. (a) Initial monolayer (ML) present (run 6). (b) Surface diffusion (run 7). (c) Surface diffusion + boundary source (run 8). The	
3.3	Representation of three finite difference methods used to solve differential equations in time (n) and space (x): (A) Crank-Nicholson, implicit method. (B) Backward Euler implicit method. (C) Forward Euler amplicit method.	25
3.4	Example of particle diffusion, where a single spike of concentration spreads over time due to diffusion. Each curve is 10% into the total duration of the simulation except the first curve, which is the starting condition. This example has $D = 1.0 \times 10^8$ Å/s, $\Delta x = 1.0$ Å, and $\Delta t = 1.0 \times 10^{-8}$ s with a total simulation duration of $1.0 \times 10^{-7}$ seconds.	20
3.5	Example of particle diffusion, where a single spike of concentration spreads over time due to diffusion. Each curve is 10% into the total duration of the simulation except the first curve, which is the starting condition. This example has $D = 1.0 \times 10^8$ Å/s, $\Delta x = 1.0$ Å, and $\Delta t = 5.0 \times 10^{-9}$ s with a	2.0
3.6	Example of particle diffusion, where a single spike of concentration spreads over time due to diffusion. Each curve is 10% into the total duration of the simulation except the first curve, which is the starting condition. This example has $D = 1.0 \times 10^8$ Å/s, $\Delta x = 1.0$ Å, and $\Delta t = 1.0 \times 10^{-9}$ s with a total simulation duration of $1.0 \times 10^{-7}$ seconds	30
3.7	The dimensionless diffusion coefficient, $D'$ , as a function of spatial step, $\Delta x$ , and time step, $\Delta t$ , for a diffusion coefficient of $1.0 \times 10^8$ Å/s. The green region defines the parameter space where the dimensionless diffusion coefficient is below 0.5 and the red above 0.5.	31
3.8	The initial precursor concentration as a function of time, (A) The concentration from two separate simulations where one is EBID and the other EBIE (B) The precursor concentration over time from a EBIED simulation	20
3.9	(Figure Replicated from Lobo, et al. [69]) (a) Growth rate plotted as a function of radius (r) from the beam axis, calculated using currents of 0.4, 0.5, 0.52, 0.53, 0.55, 0.6, 0.7, 0.8 and 1 nA. Also shown is the total electron flux profile from figure 1(d). (b) Surface plots of the 0.4, 0.5 and 0.6 nA	52
3.10	deposition rate profiles (linear scale) $(P_d = 10^{-2} \text{ Pa})$ Comparison between the continuum component of the hybrid model used here and the continuum model published previously by Lobo et al. [69]. The EBID rates were calculated at a distance of ~ 1.5 Å from of the electron beam axis as a function of electron beam current. Both models show the same decrease in growth rate with increasing current, caused by adsorbate	33
	depletion near the beam axis	34

3.11	(Replicated from David Joy, 1995[88]) The scattering path of an electron with the corresponding step length and angle components.	38
3.12	The original Parametric Model, where all secondary electrons generated are emitted through the closest surface bin.	41
3.13	The first modification to the Parametric Model, where all the secondary electrons generated are distributed evenly over the closest surface bins	42
3.14	The second modification to the Parametric Model, where all the secondary electrons generated are distribution evenly over the closest surface bins, however the number in each bin is modified by its solid angle to the primary electron trajectory.	42
3.15	Comparison between the Monte Carlo component of the hybrid model used	
	here and the Monte Carlo model CASINO [80]. The dependence of the backscattered electron coefficient on electron beam energy calculated the hybrid model is in excellent agreement with that calculated by CASINO.	44
3.16	Comparison between the secondary electron yield on a silver surface as a function of electron beam energy taken from literature data and the hybrid	
	continuum-Monte Carlo model	44
3.17	The secondary electron yield on a silver surface as a function of electron beam tilt. The two distinct trends are consistent with known behaviour of the depth and size of the electron beam interaction volume with beam tilt	45
3 18	Two EBID simulations were performed for a maximum duration of 13.7	40
0.10	seconds, each plot is shown at different stages within the entire simulation beginning at 25% through to 100% of the maximum duration. (A) Grown without surface evolution the deposit growth direction is upwards over all space; this is confirmed in (B) where the deposit structures have been nor- malised. (C) Grown with surface evolution the deposit growth is in the	
0.10	surface normal direction; again confirmed in (D)	47
3.19	The electron flux profile (primary electrons only) from an EBID simulation with electron beam projection switched on/off. The simulation maximum duration was 13.7 seconds, and each plot is shown at different stages within the entire simulation beginning at 25% through to 100% of the maximum duration. We observe as the simulation progress the electron flux profile changes in shape to reflect the evolving surface, which would be similar to	
	that shown in Figure 3.18	48
3.20	The translation between the physical surface A) and the computational surface B). The physical surface is two dimensional in $r \& z$ and the computational surface is one dimensional in $r$ , where both surfaces are radially symmetric. The path length between the points along the physical surface	
	is, <i>s</i>	49
3.21	(Figure adapted from Sobey [94]) Non-Uniform Grid Spacing Schematic	51
3.22	Realistic Non-Uniform Grid Spacing Example, Schematic.	51
3.23	The first two steps of the area remapping process required to ensure correct diffusion behaviour for an evolving surface. (1) calculate the initial surface area between each point along the flat substrate; (2) calculate the surface area between each point along the now evolving nano-structure surface. An	
	example of the calculated area between two points is highlighted in grey	52

3.24 3.25	A conical frustum is defined as a cone with the tip removed, where $R_1$ is the base radii, $R_2$ , is the top radii, $h$ is the height and $s$ is the slant height[95]. A comparison of the time-evolution of the actual volume of a deposit simu- lated by the hybrid model, and the volume expected from the total number of molecules dissociated by electrons. The two volumes are in excellent agreement, with only minor differences of <1% observed in the residuals.	53 54
4.1 4.2 4.3	EBIED Simulator Flowchart describing the general flow and order of modules. Example input text file for the EBIED Simulator	56 57 59
5.1	A series of deposits shown as a function of time and temperature, with an insert depicting the typical progression of a deposit's FWHM with time. The point where the FWHM no longer increases with time is considered standy state growth	70
5.2	Plots of $\ln(\partial h/\partial t)$ versus $1/T$ simulated using electron beam currents in the range of 0.01 pA – 1 nA in the absence of diffusion. Also shown are the corresponding straight line fits used to obtain the activation energies	15
5.3	plotted in Figure 5.6	80
5.4	analysis of EBID rates is negligible	82
5.5	temperature window $\Delta T$ in the range of 20 to 50 K.]	83
5.6	$\Theta \to 1$ Dependence of activation energy on beam current simulated in the absence of diffusion $(D_a = 0)$ and in the presence of diffusion $(D_a = D_0 e^{-E_d/(k_B T)})$ , where $E_d$ is the diffusion energy). Also shown is a plot of adsorbate deple- tion $(\Theta_{r\to 0}/\Theta_{r\to\infty})$ simulated at the beam axis $(r \to 0)$ in the absence of diffusion. The activation energy diverges from the adsorption energy $(E_a)$ of 666 meV as the extent of depletion approaches 1. The precursor pressure was 0.01 Pa and the temperature was varied from 400 to 450 K	84 85

6.1	Effects of diffusion on the shapes of deposits grown by EBID. (a) A series of deposits simulated as a function of temperature. At low temperatures	
	the deposit geometry is unaffected by diffusion, but at elevated tempera-	
	tures each deposit contains a characteristic 'ring' generated by adsorbates	
	supplied through surface diffusion. (b) Steady state vertical growth rates $(D)$ subsubted as a function of distance $(n)$ from the electron beam axis	
	(K) calculated as a function of distance (r) from the electron beam axis at a number of temperatures $(T_r)$ . All simulations were performed using a	
	Gaussian electron beam under conditions of high adsorbate depletion near	
	the beam axis. The normalized electron flux profile $f_N(r)$ is shown as a	
	dashed curve in (b).	92
6.2	(a) Steady state plots of the driving force of diffusion (c) versus distance $(r)$ from the electron beam axis at a number of temperatures $(T_n)$ . Each	
	c(r) profile contains two distinct regions corresponding to the source and sink of adsorbates that diffuse along the surface and are consumed in FRID.	
	The sink and source are separated by $r_0$ , shown as a dashed line at 125 nm.	
	(b) Corresponding adsorbate coverage profiles $(\Theta(r))$ , and the normalized	
	electron flux profile (( $f_N(r)$ , dashed grey curve)	93
6.3	(a) The fluence (C) found by integrating $c(r)$ over the sink $(0 \le r \le r_0)$	
	Shown in Figure 6.2(a), plotted for a number of temperatures $T_n$ . (b,c) Corresponding plots of $R_{VD}$ and $R_{VD}/C$ versus $T_n$ . The Arrhenius analysis	
	method yields good approximations to $E_D$ and $D_o$ at temperatures between	
	$\sim 220$ K and $\sim 275$ K	95
6.4	Arrhenius plots used to generate the data in Figure $6.5(a)$ at temperatures	0.0
6 5	$(T_n)$ of 150, 200, 250 and 300 K	96
0.0	(a) Activation energy (red) and pre-exponential factor (blue) obtained by Arrhenius analysis of $B_{VD}/C$ at a number of temperatures $T_{m}$ . The quanti-	
	ties are approximately equal to $E_D$ and $D_o$ (shown as dashed lines) over the	
	temperature window $220 \lesssim T_n \lesssim 275$ K. (b) Diffusion coefficient (D) versus	
	temperature (dashed black curve), and diffusion coefficients (red diamonds)	07
6.6	calculated using the activation energies and pre-exponential factors in (a). The fluence $C$ plotted as a function of electron beam current	97 100
6.7	Maximum flux of diffusing adsorbates $(\max[D\nabla^2 N_a(r)])$ plotted at a num-	100
0.1	ber of temperatures $T_n$ . The adsorption flux $(sF)$ is shown as a dashed	
	horizontal line.	102
6.8	Activation energy (red) and pre-exponential factor (blue) obtained by Ar- rhonius analysis of $R_{\rm energy}$ (C at a number of term protunes $T_{\rm energy}$ ). The values	
	$R_{VD}(T_n)$ was estimated by subtracting (a) $R(r, T_{min} = 120 \text{ K})$ and (a)	
	$R(r, T_{min} = 150 \text{ K})$ from each $R(r, T_n)$ profile, and integrating the resulting	
	curves over <i>r</i>	105

## List of Tables

3.1	Realistic Non-Uniform Grid Spacing Example. The fifth point was assumed	
	to be repeated in order to calculate the required data	51