

A Fundamental Investigation Into Electron Beam Induced Deposition

James Bishop

A thesis submitted to the Faculty of Science of the University of Technology
Sydney in partial fulfilment of the requirements for the degree of:

Master of Science

University of Technology Sydney, Australia

June 2012

CERTIFICATE OF AUTHORSHIP/ORIGINALITY

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: Production Note:
Signature removed prior to publication.

Acknowledgments

First of all I would like send thanks to my supervisor Professor Matthew Phillips. The broad project proposal he created allowed minimal restrictions upon my research and also for his help in many areas and in the preparation of this thesis. I would also like to thank all the staff at the Microstructural Analysis Unit of UTS: Katie Mcbean, Mark Berkahn, Richard Wuhner and Geoff McCredie for instruction with instrument usage and help in various areas. A special mention has to be given to Geoff McCredie, his help with construction of experimental apparatus and general workshop wizardry made the research possible. The ESEM cell was mostly his work and this project would not have succeeded without the equipment and apparatus which he created. Geoff taught me much about working metal and all things technical and the MAU surely could not function without him. Greg and Greg of the science workshop also provided much help with apparatus manufacturing and I would like to express my gratitude.

I would like to thank my fellow students at the MAU, Richard Crendal and Aiden Martin. Aiden deserves a special mention as he taught me much about electron microscopy, vacuum systems and experimental apparatus development. Aiden was instrumental in performing the upgrades to the XL30 ESEM and in constructing the excellent experimental apparatus which is described in the thesis. Aiden also performed the EDS compositional analysis on some of my experimental samples for me which added useful data to this thesis. It was a pleasure working with you guys and thankyou Richard for being my Australian correspondent whilst I was finishing this thesis from a dingy Spanish hotel room.

My two apprentices Chris Badawi and Douglas Gregory-Jones I would like to thank for some of the tedious work they did for me including the analysis of some experimental data. It also felt good to pass on the knowledge I have gathered and experimental procedures I developed over the course of this project concerning EBID experimentation.

I would like to thank Professor Charlene Lobo for help with EBID modelling work and creation of the main paper which was produced as a result of this project.

Above all I would like to thank Professor Milos Toth. The majority of the work of this thesis would not have been possible without the arrival of Milos at the MAU. The funding that was secured through an agreement with FEI company by the arrival of Milos at the MAU, allowed for the costly apparatus development. Milos has been an excellent role model for me as a scientist and has inspired me to want to become a scientist and make an impact in the world. Apart from that, Milos's expertise in the field of EBEID research and broad scientific knowledge allowed the maximum amount of data to be collected from each experiment. The project would surely have stumbled along blindly without help and direction from Milos.

The project was funded by the Australian Research Council (ARC) and FEI company. The ARC provided a grant which paid for my scholarship and FEI provided much of the equipment used for the research along with one of their best researchers. I would like to express gratitude to both FEI and the ARC.

TABLE OF CONTENTS

Certificate.....	ii
Acknowledgements.....	iii
Table of Contents.....	v
List of Figures.....	viii
List of Common Acronyms Used.....	xiii
List of Symbols for Common Parameters.....	xiv
Abstract.....	xvi
<u>Chapter 1: Introduction</u>	1
1.1 Electron Beam Induced Deposition and Etching.....	1
1.2 Experimental Setups for EBIED Study.....	3
1.3 The EBIED Process.....	7
1.4 Current EBID Research.....	9
1.5 Industry Potential and Practical Applications of EBIED...	15
1.6 Motivation for Research of this Thesis.....	19
<u>Chapter 2: Theoretical Aspects of EBIED</u>	21
2.1 Physical Interactions.....	21
2.2 Theoretical Model.....	30
2.3 Experimental Instrumentation Theory.....	34
2.4 Literature and Theory Most Relevant to this Thesis.....	38
<u>Chapter 3: Experimental Apparatus and Procedures</u>	41
3.1 Practical Necessities for Reliable EBIED.....	41
3.2 Initial Experimental Apparatus.....	42
3.3 Experimental Apparatus Upgrades.....	47
3.4 The “ESEM Cell”	50
3.5 Performing ESEM Cell EBID Experiments.....	54
3.6 EBID Experimental Result Analysis Procedures.....	60
<u>Chapter 4: EBID Adsorption Kinetics</u>	62
4.1 Abstract.....	62
4.2 Introduction.....	62
4.3 Experimental.....	65

4.4	Results and Discussion.....	67
	- Defocused Beam EBID.....	67
	- Defocused EBID at Room Temperature.....	69
	- Defocused EBID with Increasing T_s	72
	- Adsorption Kinetics: Studies Concerning T_s Dependence of TEOS Adsorption.....	75
	- Adsorption Kinetics: Adsorption Kinetics in General.....	76
	- Explanation of Defocused TEOS EBID Results.....	79
	- Extending Standard EBID Model to Account for Activated Chemisorption.....	81
	- Simulation Results.....	84
	- Practical Advantages of Activated Chemisorption for EBID.....	87
4.5	Conclusions.....	90

Chapter 5: FEBID with Increasing Substrate Temperature 91

5.1	Abstract.....	91
5.2	Introduction.....	91
5.3	Experimental.....	93
5.4	Results and Discussion.....	94
	- Room Temperature EBID with TEOS Precursor.....	94
	- FEBID with Increasing T_s	96
	- Explanation of Results.....	101
5.5	Conclusions.....	110

Chapter 6: TEOS EBID with Gas Mixing 111

5.1	Abstract.....	111
5.2	Introduction.....	111
5.3	Experimental.....	112
5.4	Results and Discussion.....	114
	- TEOS EBID with O_2 and Ar Mixing at RT.....	114
	- Growth Suppression with Ar Mixing.....	117
	- Growth Enhancement with O_2 Mixing at RT.....	118
	- Compositional Enhancement with O_2 Mixing.....	120
	- T_s Dependence of TEOS EBID with O_2 Mixing.....	121
	- Unique Geometry of TEOS FEBID Deposits with O_2 Mixing.....	125
	- Factors Contributing to TEOS + O_2 FEBID Pillar Geometry.....	128
5.5	Conclusions.....	131

<u>Main Conclusions of Thesis</u>	133
<u>Appendix I: Preliminary EBID Experimentation</u>	134
<u>Appendix II: EBID System Parameter Dependence</u>	144
- Factors which Affect the EBIED Process.....	144
- Electron Beam Current.....	145
- Precursor Pressure.....	147
- Acceleration Voltage.....	148
<u>Bibliography</u>	151

List of Figures

Chapter 1:

Fig. 1.1: SEM images and schematic of GIS [20].

Fig. 1.2: Schematic of GIS EBIED experimental apparatus [20].

Fig. 1.3: Schematic of sub-chamber EBIED experimental apparatus [21].

Fig. 1.4: (a.): Illustration of the EBID process. (b): Illustration of the EBIE process.

Fig. 1.5: Monte-Carlo simulated electron emission from electron beam of zero diameter [49].

Fig. 1.6: Schematic and SEM image of FE nanosized electron emitter for DEAL system [51].

Fig. 1.7: Zeiss Merit HR32 photomask repair instrument [52].

Fig. 1.8: EBID seeded CVD of $\text{Co}_2(\text{CO})_8$ precursor [56].

Fig. 1.9: Photonic band-gap structure created by EBID [57].

Fig. 1.10: Schematic of nanoparticle separator device created by EBID [58].

Fig. 1.11: SEM image showing nanoscale gated cathode FE device [61].

Fig. 1.12: SEM image showing nanoscale FE device fully fabricated by EBID [62].

Chapter 2:

Fig. 2.1: Simulated initial adsorbate coverage for Langmuir Isotherm [40].

Fig. 2.2: Simulated initial adsorbate coverage for multilayer adsorption [40].

Fig. 2.3: Representation of electron beam interaction volume within a flat substrate [70].

Fig. 2.4: Characteristic electron emission curve of a flat substrate [20].

Fig. 2.5: Cross-sections for electron induced reactions of H_2O [37].

Fig. 2.6: Estimated effective cross section for electron induced dissociation of WF_6 and simulated electron emission distribution [26].

Fig. 2.7: Illustration of the main processes which occur during EBIED.

Fig. 2.8: SEM image and simulation results for the SEBIED process [42].

Fig. 2.9: I_e curves and SEM images demonstrating in-situ EBID monitoring.

Fig. 2.10: Structure of the TEOS molecule.

Chapter 3:

Fig. 3.0: Photograph of XL30 ESEM before upgrades.

Fig. 3.1: Illustrations of ESEM operating principles.

Fig. 3.2: Photograph of PDS for preliminary experimentation.

Fig. 3.3: Photograph of interior of XL30 ESEM Specimen Chamber.

Fig. 3.4: Photos of upgrades and new equipment.

Fig. 3.5: Schematic and photo of new PDS and photo of VCR components.

Fig. 3.6: Photos of ESEM cell sub-chamber.

Fig. 3.7: Simple cross-sectional schematic of the ESEM cell.

Fig. 3.8: Images of upgraded EBIED equipment.

Fig. 3.9: Images of N_2 glove box and precursor crucible.

Fig. 3.10: Typical beam current profile.

Fig. 3.11: Schematic of XL30 ESEM vacuum system.

Fig. 3.12: (a): Typical I_e and I_t curves. (b): I_t curve indicating process error and SEM image of error.

Fig. 3.13: Photos of Zeiss LEO SEM and substrate holders.

Fig. 3.14: SEM images taken with Zeiss LEO SEM.

Fig. 3.15: BSE image of cement paste and 20 kV SEM image of EBID deposits.

Fig. 3.16: High contrast SEM image for volumetric analysis of EBID deposits and binary image used for input to volume estimation program.

Chapter 4:

Fig. 4.01: Schematic of EBID experimental apparatus.

Fig. 4.02: Schematic illustrating focused and defocused electron beams.

Fig. 4.1: Functions which approximate electron flux profiles for EBIED modelling.

Fig. 4.2: Growth rate vs beam diameter.

Fig. 4.3: Results of simple model of BSE yield.

Fig. 4.4: I_t curves of set grown as function of beam diameter.

Fig. 4.5: SEM images of defocused EBID set grown as function of T_s .

Fig. 4.6: Defocused EBID growth volume vs T_s .

Fig. 4.7: Reaction co-ordinate diagram for physisorption.

Fig. 4.8: 2D potential surface diagram.

Fig. 4.9: Reaction co-ordinate diagram for activated chemisorption.

Fig. 4.10: Illustration of dissociative chemisorption of TEOS.

Fig. 4.11: Adsorption states and transitions accounted for by extended model.

Fig. 4.12: Simulation results from extended model.

Fig. 4.13: Effect of various model parameters.

Fig. 4.14: EDS compositional analysis, C:O ratios.

Chapter 5:

Fig. 5.1: Summary of EBID with TEOS at room temperature.

Fig. 5.2: SEM images & I_e curves of TEOS FEBID deposits grown as function of T_s .

Fig. 5.3: SEM images & I_e curves TEOS FEBID deposits, function of T_s , higher range.

Fig. 5.4: SEM images of TEOS FEBID deposits grown as function of T_s .

Fig. 5.5: I_e and I_t curves of TEOS FEBID deposits grown as function of T_s .

Fig. 5.6: Schematic overlay on SEM images of EBID deposit at $T_s \gg RT$.

Fig. 5.7: Schematic of diffusion path length.

Fig. 5.8: SEM image and I_t curves of FEBID deposits grown at high T_s .

Fig. 5.9: SEM image of FEBID deposits grown as function of T_s .

Fig. 5.10: SEM image of FEBID deposits grown as function of T_s with higher P_{TEOS} .

Chapter 6:

Fig. 6.0: Schematic of gas mixing PDS.

Fig. 6.1: SEM images & volume vs time of TEOS EBID deposits with O_2 & Ar mixing.

Fig. 6.2: SEM images & volume vs time of TEOS EBID deposits with O_2 & Ar mixing, grown as function of beam diameter.

Fig. 6.3: SEM image of EBID deposits grown for EDS analysis.

Fig. 6.4: EDS compositional analysis results.

Fig. 6.5: SEM images and volume vs T_s for TEOS EBID with and without O_2 mixing.

Fig. 6.6: Reaction co-ordinate diagram representing possible adsorption states.

Fig. 6.7: SEM image showing unique geometry of FEBID using TEOS + O_2 .

Fig. 6.8: SEM images and I_t curves of TEOS + O_2 FEBID deposit grown for long t_g .

Fig. 6.9: Volume vs t_g for TEOS + O_2 FEBID.

Fig. 6.10: SEM images of TEOS + O_2 FEBID deposits, function of I_b .

Appendix I:

Fig. AI.1: 3D AFM image of rectangular carbonaceous EBID deposit.

Fig. AI.2: 3D AFM images of pillar and ring carbonaceous EBID deposits.

Fig. AI.3: 3D AFM image and SEM image of carbonaceous EBID pillars with depression in the middle.

Fig. AI.4: SEM image of TEOS FEBID pillars, function of I_b .

Fig. AI.5: SEM image of FEBID deposits using residual TEOS as precursor.

Fig. AI.6: SEM image of substrate after TEOS condensed on surface.

Fig. AI.7: EBID deposits from liquid phase TEOS.

Appendix II:

Fig. AII.0: EBIED mind map.

Fig. AII.1: SEM images of FEBID deposits, function of I_b .

Fig. AII.2: SEM image & volume vs P_{TEOS} for FEBID deposits, function of P_{TEOS} .

Fig. AII.3: SEM images and volume vs Δd_{f-s} for 2 sets of FEBID deposits grown at different V_0 .

Fig. AII.4: Growth regions of standard FEBID pillar.

Fig. AII.5: SEM image of FEBID deposits, function of V_0 .

List of Commonly Used Acronyms

- AFM – Atomic force microscopy.
AOCVD – Atomic oxygen induced chemical vapour deposition.
BSE – Backscattered electron.
CID – Collision induced desorption.
CIM – Collision induced migration (impact enhanced diffusion).
CIP – Collision induced processes.
CL – Cathodoluminescence.
CNT – Carbon nanotube.
CVD – Chemical vapour deposition.
D – Deposit.
DEAL – Digital electrostatic array lithography.
EBID – Electron beam induced deposition.
EBIE – Electron beam induced etching.
EBIED – Electron beam induced etching and deposition.
EBIH – Electron beam induced heating.
EBL – Electron beam lithography.
EDS – Energy dispersive x-ray spectroscopy.
EL – Electron limited.
ESD – Electron stimulated desorption.
ESEM – Environmental scanning electron microscope.
EUV – Extreme ultraviolet.
FE – Field emission.
FEBID – Focused electron beam induced deposition.
FEG – Field emission gun.
GIS – Gas injection system.
GSED – Gaseous secondary electron detector.
HIVAC – High Vacuum.
HV – High vacuum.
IC – Integrated circuit.
KE – Kinetic energy.
LAOCVD – Localised atomic oxygen induced chemical vapour deposition.
MFC – Mass flow Controller.
MTL – Mass transport limited.
NI – National Instruments.
ODP – Oil diffusion pump.
PBG – Photonic band-gap.
PD – Partially depleted.

PDS – Precursor delivery system.
PE – Primary electron.
PECVD – Plasma enhanced chemical vapour deposition.
PVP – Pre-vacuum pump.
RGA – Residual gas analysis.
RT – Room temperature (≈ 300 K).
S2N – Signal to noise (ratio).
SE – Secondary electron.
SEBIED – Simultaneous electron beam induced etching and deposition.
SEM – Scanning electron microscopy.
STEM – Scanning transmission electron microscopy.
STM – Scanning tunnelling microscopy.
TC – Thermocouple.
TEM – Transmission electron microscopy.
TEOS – Tetraethoxysilane.
TMP – Turbo molecular pump (high vacuum pump).
TPD – Temperature programmed desorption.
UHV – Ultra high vacuum.
UV – Ultraviolet.
UVPL – Ultraviolet photolithography.
VACNF – Vertically aligned carbon nanofibers.
VCR – Vacuum coupling radiation (High vacuum fittings).
XPS – X-ray photoelectron spectroscopy.

Symbols for Commonly Referred Parameters/Species

e^- – Electron.
 T_s – Substrate temperature.
 T_g – Gas temperature.
 t_g – Growth time.
 I_b – Electron beam current.
 I_e – Emitted current.
 I_t – Transmitted current.
 P_T – Total pressure in cell.
 P_{TEOS} – TEOS partial pressure.
 P_{O_2} – O_2 partial pressure.
 O^\cdot – Atomic oxygen (radical).
 σ – Effective cross-section for electron induced dissociation.
 D – Diffusion co-efficient.

List of Common Acronyms and Parameter Symbols

τ – Residence time.

L_d – Mean diffusion length.

V_0 – Acceleration voltage.

Abstract:

Electron beam induced deposition (EBID) is a maskless, direct-write nanofabrication technique. It is capable of very high resolution and deposition of a wide variety of materials. It is a widely used technique for nanoprototyping and has several current applications in industry including the repair of photolithographic masks for integrated circuit (IC) production. Despite the widespread usage of EBID, the fundamental mechanisms which govern the process are not sufficiently well understood.

In this thesis, an experimental-based investigation is undertaken in order to obtain a greater understanding of fundamental factors which govern the EBID process and particularly those factors not accounted for by current models of EBID. A world-class and possibly unique experimental apparatus is developed which allows quantitative EBID experimentation. The conclusions reached demonstrate the importance of a previously neglected fundamental aspect of EBID: the adsorption kinetics of precursor molecules. The findings have significant importance for EBID and the sister technique of electron beam induced etching (EBIE).

The first chapter presents a thorough general background and introduction to electron beam induced etching and deposition (EBIED) and literature review with a focus on EBID. Chapter two discusses theoretical aspects of EBIED and current models. Chapter three is a record of the apparatus and experimental procedures which were developed and can be considered as a recipe for reliable EBID experimentation.

Experiments were performed as a function of substrate temperature in chapters four and five. The results which were not predicted by current models of EBID demonstrate the effect of activated chemisorption. A new model is developed which correctly predicts the generic temperature dependence of the EBID process. Activated chemisorption is found to allow simultaneous high purity and high growth rates of EBID deposits. EBID at high T_s with TEOS precursor was found to result in complex unexpected growth and mechanisms involving diffusion, electron beam induced heating (EBIH) and charging are presented and discussed to explain this growth in chapter five.

Chapter six involves TEOS EBID with gas mixing. The growth rate was found to be significantly enhanced or suppressed with O_2 or Ar mixing respectively. A new mechanism (termed LAOCVD) is proposed to explain O_2 mediated purity and EBID rate enhancement with organosilane precursors as reported in literature and demonstrated by my results. The effects of EBID system parameters are characterised and explained in the appendix.