A Fundamental Investigation Into Electron Beam Induced Deposition

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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.

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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_{O2} – O_2 partial pressure.
$O^{\cdot}$ – Atomic oxygen (radical).
σ – Effective cross-section for electron induced dissociation.
D – Diffusion co-efficient.

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 EBIED process and particularly those factors not accounted for by current models of EBIED. 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. FEBID 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.