

# **Electron Beam Heating Effects During 3D Nanoprinting Using Focused Electron Beam Induced Deposition**

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## **Dedication**

*To my grandmother Phoebe Ndemange*

*and*

*To all who *The Fog* renders the mundane insurmountable*

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## Abstract

Focused electron beam induced deposition (FEBID) is a promising additive nanomanufacturing tool which has recently advanced from a trial-and-error experimental method to a controlled, predictable, and simulation-guided 3D nanoprinting technology. FEBID uses a finely focused electron probe to dissociate surface adsorbed precursor molecules resulting in a highly localized mesh style deposit. The mesh objects are constructed using interconnected nanowires, where the final shape of the 3D nanostructure is wholly dependent on the precision of the individual nanowires. However, these nanowires are prone to deflections and tapering effects, and thus 3D FEBID technology is precision limited.

Here, the precision limiting effect has been quantified. Complementary experiments, models, and simulations identified that electron beam induced heating influenced the deposition rate during the direct-write process. The beam interaction driving deposition simultaneously triggers local heating. As the nanowire elongates, thermal resistance increases, and the temperature gradually rises at the beam impact region (BIR). The heat generated must flow through the 3D nanostructure to the heat sink, that is, the substrate. This process mimics the classical heat transfer through fins.

Simulations uncovered that the beam heating impacts the Arrhenius precursor surface residence time ( $\tau(T)$ ) such that, the rate of precursor desorption increases and consequently, the rate of deposition goes down. It was found that the vertical growth rate

decreases and results in nanowire tapering and deflection with increasing length, even for temperature increments in the order of 10 K.

## Table of Contents

|                                                                   |    |
|-------------------------------------------------------------------|----|
| Chapter 1 : Introduction .....                                    | 1  |
| 1.1 Motivation.....                                               | 1  |
| 1.2 3D Nanoprinting Technologies.....                             | 2  |
| 1.3 Objectives .....                                              | 6  |
| 1.4 Outline of Work .....                                         | 6  |
| Chapter 2 : Literature Review .....                               | 8  |
| 2.1 Development of Focused Electron Beam Induced Deposition ..... | 8  |
| 2.2 A Review of Electron Beam Induced Heating.....                | 17 |
| 2.2.1 Electron Scattering.....                                    | 20 |
| 2.2.2 Electron Beam Induced Heating .....                         | 23 |
| 2.2.3 Semi-Infinite Substrate Geometry .....                      | 24 |
| 2.2.4 Thin-Film Geometry .....                                    | 25 |
| 2.2.5 3D FEBID Nanostructures .....                               | 26 |
| Chapter 3 : Materials and Methods .....                           | 30 |
| 3.1 Electron Beam Parameters.....                                 | 31 |
| 3.1.1 Beam Acceleration Energy and Beam Current.....              | 31 |
| 3.1.2 Beam Focus.....                                             | 34 |
| 3.1.3 Gas Injection System .....                                  | 37 |
| 3.1.4 Electron Beam and GIS Experiment Set-up .....               | 38 |
| 3.2 Sample Current Collection.....                                | 41 |
| 3.3 FEBID Computer Aided Design Program (3BiD).....               | 41 |
| Chapter 4 : Results .....                                         | 45 |
| 4.1 Single Calibration Structure.....                             | 45 |
| 4.1.1 Pillar.....                                                 | 47 |
| 4.1.2 Transition .....                                            | 48 |
| 4.1.3 Segment.....                                                | 48 |
| 4.2 Calibration Structure Array.....                              | 50 |
| 4.3 Calibration Structures at 30 keV and 7.5 keV .....            | 53 |

|                                                                 |                                                                              |     |
|-----------------------------------------------------------------|------------------------------------------------------------------------------|-----|
| 4.4                                                             | Sample Current Characterization .....                                        | 55  |
| 4.5                                                             | Sample Current Data for a Single Calibration Structure .....                 | 59  |
| 4.6                                                             | Sample Current Traces for an Array of Calibration Structures .....           | 61  |
| 4.7                                                             | Sample Current Traces for Calibration Structures at 30 keV and 7.5 keV ..... | 64  |
| 4.8                                                             | 3D FEBID Calibration Structure and Sample Current Simulations .....          | 68  |
| Chapter 5 : Discussion .....                                    |                                                                              | 71  |
| 5.1                                                             | Effects of Electron Beam Interaction Volume .....                            | 71  |
| 5.2                                                             | Sample Current Equations .....                                               | 73  |
| 5.3                                                             | 7.5 keV and 30 keV Sample Current .....                                      | 74  |
| 5.4                                                             | Electron Capture via Ga <sup>+</sup> Milled Substrate .....                  | 76  |
| 5.5                                                             | A Sample Current Trace Artifact .....                                        | 79  |
| 5.6                                                             | 1D Beam Induced Heating Analysis .....                                       | 81  |
| 5.7                                                             | Characteristics of Beam-Induced Heating via 1D Model .....                   | 86  |
| 5.8                                                             | Heat Transfer from Inelastic Energy Loss .....                               | 92  |
| 5.9                                                             | The Absorption Thicknesses .....                                             | 93  |
| 5.10                                                            | Cross-Sectional Area Variation .....                                         | 95  |
| 5.11                                                            | Temperature Dependent Properties .....                                       | 96  |
| 5.12                                                            | Finite Difference Approximation at Deposit-Substrate Boundary .....          | 99  |
| 5.13                                                            | 3D FEBID Simulations Confirm Heating Results .....                           | 103 |
| 5.13.1                                                          | Electron-Limited Regime (ELR) .....                                          | 105 |
| 5.13.2                                                          | Precursor-Limited Regime (Refresh) .....                                     | 105 |
| 5.13.3                                                          | Diffusion-Enhanced Regime (DER) .....                                        | 106 |
| 5.13.4                                                          | DER with Active Beam Induced Heating .....                                   | 106 |
| 5.13.5                                                          | Reduced Diffusion Coefficient .....                                          | 107 |
| 5.14                                                            | Heat Compensation .....                                                      | 107 |
| Chapter 6 : Conclusion and Future work .....                    |                                                                              | 110 |
| References .....                                                |                                                                              | 112 |
| Appendices .....                                                |                                                                              | 124 |
| Appendix A: 1D Beam Heating Model – T vs s .....                |                                                                              | 125 |
| Appendix B: 1D Beam Heating Model – T <sub>max</sub> vs S ..... |                                                                              | 135 |

|           |     |
|-----------|-----|
| Vita..... | 137 |
|-----------|-----|

## List of Figures

|                                                                                                                                                                                                                                                                                                                                                                   |    |
|-------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|----|
| Figure 1-1 Capabilities and features of various metal micro/nano additive manufacturing technologies. a) A comparison of geometrical capabilities of each technique. b) Patterning speed versus x-y feature size of all techniques [11]. .....                                                                                                                    | 5  |
| Figure 2-1 Shawinigan Acetylene Black under continuous electron collision in the electron microscope. Collision times (top left to bottom right) are: zero; 1 min.; 2 min.; 3 min.; 4 min.; 5 min.; 7 min.; 9 min.; 11 min.; 12 min. relative to the first exposure [15]. .....                                                                                   | 9  |
| Figure 2-2 Christy's model of electron-beam-induced deposition. R: deposition rate. v: molecular volume. F: precursor flow. $\sigma$ : cross-section of electron induced fixation. $\tau$ : precursor residence time at the surface. f: electron flow. a: molecule. V: area. N: precursor surface density [18,19]. .....                                          | 10 |
| Figure 2-3 Illustration of 3D contaminant growth with decreasing beam size and contamination rods deposited by a lateral scanning beam. ....                                                                                                                                                                                                                      | 12 |
| Figure 2-4 A demonstration of predictive and control capabilities of FEBID simulations. (a) and (c) compare electron micrograph images from experiments with virtual SEM images obtained from simulations. (b) Simulated secondary electron scattering events and morphology during 3D FEBID [37]. .....                                                          | 15 |
| Figure 2-5 A deposited 3D plasmonic tetragonal bipyramid structure and its plasmonic response during electron energy loss spectroscopy measurements [45]. .....                                                                                                                                                                                                   | 16 |
| Figure 2-6 The increase of substrate temperature as a function of electron beam current and the thermal conductivity k, of the substrate [46]. .....                                                                                                                                                                                                              | 19 |
| Figure 2-7 Electron range in bulk PtC <sub>5</sub> estimated using the Kanaya–Okayama formula (Equation 2-4) for the typical FEBID primary electron energy range. ....                                                                                                                                                                                            | 22 |
| Figure 2-8 (a) Comparison of simulations with analytical estimation given by Equation 2-7. A SiO <sub>2</sub> pillar with 100 nm diameter irradiated by a 20 keV, 500 pA beam. Inset: 30 electron trajectories at pillar lengths of 20, 100, and 300 nm showing the shift of the interaction volume from the substrate into the pillar. (b) Arrhenius plot of the |    |

|                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                |    |
|----------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|----|
| SiO <sub>2</sub> deposition rate as a function of temperature. Deposition rate decreases with increase in temperature [47,56].....                                                                                                                                                                                                                                                                                                                                                                             | 28 |
| Figure 2-9 Effects of temperature rise on FEBID nanostructures. Morphology and composition change due to a temperature gradient along a horizontal freestanding nanorod. EDXS indicates increasing Cu metal content in the deposits, with increasing crystal size [49,57].....                                                                                                                                                                                                                                 | 29 |
| Figure 3-1 Tilted SEM images of calibration structure arrays deposited at different primary electron energies and currents (indicated on image top right). Co-deposits and co-branches marked by yellow and red circles, respectively [59]. ....                                                                                                                                                                                                                                                               | 33 |
| Figure 3-2 Top: Tilted SEM images of vertical pillars showing electron beam defocus effects. Beam defocus is increased from left to right. Bottom: The evolution of Pt pillar diameters (circles) and heights (squares) for focused (open symbols) and 20 $\mu$ m defocus (filled symbols) conditions. Experimental conditions: 30 keV, 150 pA, 4 ms dwell time, 28 ms refresh time [61]. ....                                                                                                                 | 36 |
| Figure 3-3 3D FEBID experimental set up. Thermo Fisher Scientific Gas injection system components and an electron micrograph of the GIS nozzle on ‘insert’ position inside the Nova600™ dual beam system. Scale bar = 0.5 mm.....                                                                                                                                                                                                                                                                              | 39 |
| Figure 3-4 The front panel of a Keithley Model 6485 Picoammeter used to collect sample current during FEBID. ....                                                                                                                                                                                                                                                                                                                                                                                              | 43 |
| Figure 3-5 3BiD [38] CAD Graphical user interface for 3D FEBID design and exposure file generation. The features highlighted are (1) the $\zeta$ vs $\tau_d$ calibration file, (2) vertices and vertex-vertex interconnects assignment tabs, (3) 2D and 3D design view panels, and (4) exposure level sequence toggle panel.....                                                                                                                                                                               | 44 |
| Figure 4-1 Pillar evolution during FEBID and the accompanying sample current trace collected via the sample stage. Dash arrows point to each pillar’s current trace. A conical tip on a conical shaped is observed as the pillar height increases. The pillars are deposited by a 30 keV 32 pA beam. The design and (measured) pillar heights from left to right are: 50 (86), 100 (159), 150 (204), 200 (245), 250 (286), 300 (340), 350 (390), 400 (449), 450 (489), 500 (521), 550 (562), 600 (598) nm. The |    |

- secondary electron image was acquired at a substrate tilt angle of  $52^\circ$  in order to see the cross-sectional profile of the nanostructure. Scale bar = 200 nm. ....46
- Figure 4-2 (a) An electron micrograph of a calibration structure with a segment angle of  $\zeta = 30^\circ$ , acquired at an angle of  $52^\circ$  with respect to the substrate surface normal. The pillar = 400 nm and total projected segment length,  $b_{x,y} = 1000$  nm. The segment element is aligned with the tilt axis in the image. The discrepancy between the design and deposit is realized as a downward deflection of the segment with respect to the linear design shown by the superimposed yellow dash line and arrows. The blue double arrows indicate the decrease of vertical segment thickness with increase in segment length. (b) A plot of the vertical segment thickness,  $b_z$  variation with elongation. Inset: Changing  $\zeta$  along the projected segment length;  $\zeta = \text{atan}(b_z/b_{x,y})$ . ....49
- Figure 4-3 (a) SEM image of a calibration structure array at  $52^\circ$  tilt view. Pillar = 400 nm, segment = 400 nm, and segment angles ( $\zeta$ ) ranging from  $12.5^\circ$  to  $80^\circ$ , and  $\zeta$  is indicated on the image. The order of deposition is randomized. The yellow circle marks the last beam impact region (BIR) where the segment terminates. (b) Vertical segment thickness measured at 0 nm to 400 nm projected segment length with 50 nm increments for  $\zeta = 12.5^\circ$ ,  $25^\circ$  and  $50^\circ$ . Scale bar = 400 nm. ....52
- Figure 4-4 Arrays of calibration structures deposited at 30 keV 32 pA and 7.5 keV 37 pA highlighting effects of energy-dependent electron interaction volume, such as deposit shape, (indicated by arrows for the pillars and yellow dash circles on the segment) and deposit growth rate (marked in red). Both SEM images were captured at the same field of view at  $52^\circ$  stage tilt. Prescribed design parameters for pillar height and segment length = 400 nm. Scale bar = 400 nm. ....54
- Figure 4-5 3D FEBID illustration of a rectangular prism CAD design model, the subsequent experimental deposit and *in situ* stage sample current collected during deposition using 30keV 32 pA beam. In (a) and (b) the colors on the CAD design represent exposure levels; blue (level 1), light blue (level 2), yellow (level 3), and red (level 4). The SEM images show the final deposits. The top images are captured from a top-down view and images at the bottom from  $52^\circ$  stage tilt. The prism is

oriented at  $45^\circ$  on the supporting pillar. Length = 400 nm, width = 200 nm, height = 200 nm, and a diagonal across the short face of the prism. (a) Demonstrates poor CAD design replication due to incorrect exposure level assignment, and (b) shows accurate design replication. (c) Traces of sample current collected during deposition of (a) – red and (b) – grey. Scale bar = 200 nm. ....58

Figure 4-6 A pillar and segment calibration structure. The stages of deposition are ‘pillar’, ‘transition’ and ‘segment’. Pillar deposition occurs using stationary electron beam exposure. The electron beam moves at constant, digital beam velocity during ‘transition’ and ‘segment’ growth. The pillar and segment are both 400 nm in length. (a) An electron micrograph of a calibration structure (scale bar = 300 nm) acquired at an angle of  $52^\circ$  with respect to the substrate surface normal. (b) False color image of (a) to point out the three distinct growth stages also captured in (c). Experiments were conducted using a beam acceleration voltage of ( $E_o$ ) 30 keV and a beam current of ( $i_b$ ) 32 pA. (c) The sample current ( $i_s$ ) collected through the substrate during FEBID is sensitive to geometric changes during growth. The continuous black sample current profile was collected during deposition of (a) that yielded a segment angle of  $\zeta = 30^\circ$ . ....60

Figure 4-7 Segment angle changes are resolved in time–dependent sample current profiles collected during FEBID. In each experiment, a 400 nm pillar was deposited followed by the deposition of a segment 400 nm long; the so–called ‘calibration structure’ using  $E_o = 30$  keV and  $i_b = 32$  pA. Only the segment angle ( $\zeta$ ) was varied among the experiments. Each angle dependent profile has been shifted along the y–axis to create a separation of  $\Delta i_s = 2$  pA between each profile to avoid profile overlap and clarify trends. The sample current profile collected for the case of  $\zeta = 12.5^\circ$  was not shifted and provides a true sample current profile. The 3BiD [38] specified segment angle is shown for each curve followed by the measured value of ( $\zeta$ ) after deposition. ....63

|                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                          |    |
|----------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|----|
| Figure 4-8 A comparison of sample current traces collected during calibration structure array deposition shown in Figure 4-4. Each calibration structure total length was ( $S = 800$ nm) with a 400 nm length pillar and a 400 nm segment. ....                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                         | 66 |
| Figure 4-9 Electron interaction volume effects in 3D FEBID. Segment width is measured across the segment from a top-down view on the SEM images. Segment width increases with increasing ( $\zeta$ ), and more generally, with decreasing electron beam energy. The electron micrographs are the top-down view images of Figure 4-4. Scale bar = 400 nm. ....                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                            | 67 |
| Figure 4-10 3D FEBID calibration structure and sample current simulations using 30 keV 32 pA and 7.5 keV 37 pA primary electrons. The simulations are generated using the 3BiD CAD [38] environment and the supplementary Simulation package [37]. The virtual calibration structures are designed such that the pillar = 400 nm and segment = 800 nm at $\zeta = 30^\circ$ and $\zeta = 60^\circ$ . (a) $\zeta = 30^\circ$ at 7.5 keV, (b) $\zeta = 60^\circ$ at 7.5 keV, (d) $\zeta = 30^\circ$ at 30 keV and (e) $\zeta = 60^\circ$ at 30 keV are virtual SEM images of the calibration structure cross-section sliced along the total structure length ( $S$ ), and (Inset) normal to the segment element. The cross-sections reveal the beam-deposit interaction volume. (c) $E_o = 7.5$ keV, and (f) $E_o = 30$ keV are the sample current traces dictated by the secondary electron (SE) yield. The SE yield traces along the deposit during growth at (g) 30 keV and (h) 7.5 keV for $\zeta = 30^\circ$ are shown. Inset scale bar = 50 nm. .... | 70 |
| Figure 5-1 (a) Top down view SEM image of the SE capture experiments. The milled depths are notated on the image. A decrease in contrast of the milled trenches indicates increase in depth. (b) $52^\circ$ tilted view of (a) showing the pillar aligned to the trench edge. The control calibration structure is deposited on un-milled substrate (red). (c) Collected sample current traces during deposition. (d) The $i_s$ slopes ( $di_s/dt$ ) of the segment element showing variation with trench depth. For all the segments; $\zeta = 30^\circ$ , pillar = 400 nm, segment = 400 nm. For the trenches; length = 1 mm, width = 250 nm. Scale bar = 500 nm. ....                                                                                                                                                                                                                                                                                                                                                                                 | 78 |

- Figure 5-2 Sample current trace slopes calculated over segment growth for 30 keV and 7.5 keV data in represented in Figure 4-8. The error bars indicate the deviation from the average  $\Delta i_s/\Delta t$  calculated for each data point along a selected current trace. ..80
- Figure 5-3 The segment angle ( $\zeta$ ) is implicitly included in the 1D beam heating model by using a cross-sectional area function  $A(s)$  that varies over the pathlength ( $s$ ) of the deposit. The influence of thermal resistance as a function of segment angle is thus included. The average cross-sectional area of the pillar element is  $A_p$  and  $A_s$  for the segment and are the critical parameters dictating the thermal resistance. For  $E_o = 30$  keV and 32 pA,  $A_p = 2830 \text{ nm}^2$  and  $A_s(\zeta) = A_p(1 - e^{-\zeta/(30-0.2\zeta)})$ , where  $\zeta$  is in degrees. ....83
- Figure 5-4 The maximum temperature of the deposit as a function of the total deposit height along the  $z$ -coordinate predicted by the 1D mathematical model for  $E_o = 30$  keV and  $i_b = 32$  pA. The maximum temperature always occurs at the beam-impact region, or BIR. For the  $\zeta = 12.5^\circ$  case; (\*) indicates the transition stage between pillar and segment growth and (\*\*) shows the completion of deposition. ....88
- Figure 5-5 (a) 1D beam heating model predictions of the BIR temperature versus pathlength ( $s$ ) along the deposit. The slope of these curves (b) in the segment growth stage,  $s > 400$  nm shows the relative influence of the thermal resistance ( $R_T$ ) and the beam induced heating rate ( $q_b$ ). The color of each data point is referenced to each segment based on the segment angle ( $\zeta$ ). ....91
- Figure 5-6 (-) The temperature-dependent surface residence time  $\tau(T)$  of  $\text{MeCpPt}^{\text{IV}}\text{Me}_3$  on  $\text{SiO}_2$  [75].  $k_o = 1013 \text{ Hz}$  and  $E_a = 669 \text{ meV}$ . Based on simulations  $\tau(T)$  is updated for the  $\text{MeCpPt}^{\text{IV}}\text{Me}_3\text{-PtC}_x$  interface which controls 3D FEBID [74].  $E_a$  is updated to a value of 0.62 eV (--) that produced simulation results which predicted 3D FEBID experiments. It is estimated to be the  $E_a$  for the  $\text{MeCpPt}^{\text{IV}}\text{Me}_3\text{-PtC}_x$  interface. In comparison to  $\tau(T)$ , surface diffusion  $D(T)$  is less sensitive to temperature changes (-) [76].  $D_o = 42 \text{ mm}^2/\text{s}$  and  $E_{a(D)} = 122 \text{ meV}$ . ....98
- Figure 5-7 A schematic representing the Taylor series expansion variables and coefficients .....100

Figure 5-8 (a) Sample current traces for the calibration structure *transition* and *segment* at  $E_o = 30$  keV and  $i_b = 32$  pA under the following simulated conditions: electron-limited ‘ELR’, precursor-limited ‘Refresh’, diffusion-enhanced ‘DER’ regimes, no surface diffusion ‘No Diffusion’, and electron beam heating ‘DER (Heat)’. An experimental data set for a complementary calibration structure (●) is provided for reference.  $\zeta = 17^\circ$  for the experiment and  $\zeta = 15.6^\circ$  for the simulation. (b) Temperature map for the ‘DER (Heat)’ with beam heating applied at the BIR. Pillar = 400 nm and segment = 800 nm.....104

Figure 5-9 (a) 3D-FEBID virtual SEM image of a simulated as-deposited calibration structure exhibiting tapering and deflection. The dwell time per pixel  $\tau_d = 8.20$  ms for segment deposition,  $E_o = 30$  keV,  $i_b = 32$  pA. (b) A complementary heat compensated calibration structure deposited with varying dwell times,  $\tau_d = 8.20 - 13.10$  ms. (c) Temperature plot along the deposit axis of (a)-blue and (b)-orange. (d) Sample current trace during deposition of (a) and (b). Inset: Segment cross-section virtual image viewed parallel to  $s(x,y,z)$  calibration structure axis. Pillar length = 200 nm, segment length = 800 nm and a segment angle of  $\zeta = 30^\circ$ . Inset scale bar = 50 nm. ....109

# Chapter 1: Introduction

## 1.1 Motivation

Additive manufacturing has greatly transformed the design and production of macroscale components by enabling rapid prototyping and on-demand fabrication of customized products. Innovative products such as personalized dental and medical devices, [1] aerospace and automotive components, [2] and additively manufactured construction components [3] have benefited from additive manufacturing or 3D printing of geometries that were expensive to produce or simply not possible with traditional subtractive processes. Furthermore, 3D printed architectures are designed for best performance rather than ease of manufacturing. Similarly, nanoscale manufacturing techniques that rapidly fabricate and test new concepts are crucial for accelerating advancement in nanotechnology.

For a long time, nanoscale fabrication has depended on photolithography which has mostly evolved by using increasingly shorter wavelengths, [4] and on electron beam lithography (EBL) which offers high resolution [5]. Nanofabrication using photolithography and EBL is a subtractive process that relies on exposures of polymer thin films. These technologies are planar and 2D in nature which limit design complexity. Conversely, 3D Nano printing technologies allow the fabrication of complex geometries with overhangs/undercuts, internal spaces, open mesh, and honeycomb structures where the new limit of design is imagination.

## 1.2 3D Nanoprinting Technologies

Truly 3D nanoscale additive manufacturing technologies are those that directly add material in the desired final shape with sub 100 nm resolution without need for subtractive removal. These techniques face two main challenges: 1) nanofabrication techniques manipulate few atoms or molecules at a time and slight deviations during processing can lead to structure failure or poor design replication, and 2) the ability to manufacture nanoscale structures at a large scale with great accuracy, high resolution and with a wide range of materials.

Currently, there are various techniques that are used to print 3D nanostructures. Engstrom et al. [6] categorized additive nanomanufacturing into two major groups: direct write and single particle placement technologies. Single particle placement technologies either create structures one atom at a time or place nano-objects in a designated framework. Scanning tunneling microscopy [7], atomic force microscopy [8] and optical tweezers [9] are some of the technologies that enable single particle placement and could be the gateway to quantum computing, however, they suffer from very low throughput. Direct write technologies employ a computer-controlled translation of a pattern generating device [10] like laser writing optics, ink deposition nozzle, or focused electron/ ion beam. Direct write allows the design and rapid fabrication of complex 3D shapes without lithographic masks. These technologies also enable design and materials flexibility, high resolution, and higher throughput compared to single particle placement and are, therefore, in the forefront of 3D nano printing technologies.

Some of the current submicron scale direct write technologies of metallic structures include:

- Force-controlled electroplating (FCEP) which utilizes hollow atomic force microscopy cantilevers to dispense metal ions in a 3-electrode electrochemical cell [11].
- Direct ink writing (DIW) where metal nanoparticle inks are extruded from a glass pipette with a micron size nozzle [12].
- Electrohydrodynamic redox printing (EHD-RP) produces solvated metal ions within the printing nozzle and forms a metallic deposit once dispensed on a substrate [13].
- Femtosecond projection two photon lithography (FP-TPL) is the focusing of ultrafast laser beams for local solidification of a photoresist to achieve complex 3D structures with submicron resolution [14].
- Laser-Assisted Electrophoretic Deposition traps and collects nanoparticles in its focal spot by utilizing a finely focused laser beam to target a suspension of negatively charged metallic nanoparticles [15].
- Focused electron/ion beam induced deposition (FEBID/ FIBID) is the electron or ion beam induced dissociation of a suitable precursor to deposit a highly localized nanostructure [16-18].

Hirt et al. [19] summarized direct write additive nanomanufacturing of metallic structures and identified technologies that meet the criteria for widespread use in 3D nano printing such as patterning speeds, minimum feature size, and wide range of available printing materials with broad applicability (Figure 1-1). FEBID was found to be superior in geometric flexibility, feature size, range of deposited and substrate materials.

Focused electron beam induced deposition is usually done in a scanning electron microscope retrofitted with a gas injection system which introduces a precursor gas into the microscope. The injected precursor gas dynamically physisorbs and chemisorbs on the substrate, diffuses, and desorbs to reach an equilibrium surface coverage. The electron beam decomposes the precursor molecules leading to deposition of non-volatile fragments onto a substrate and creates highly localized functional deposits whose size, shape, and position can be controlled with nanometer scale precision. This direct write technique is the focus of this thesis.

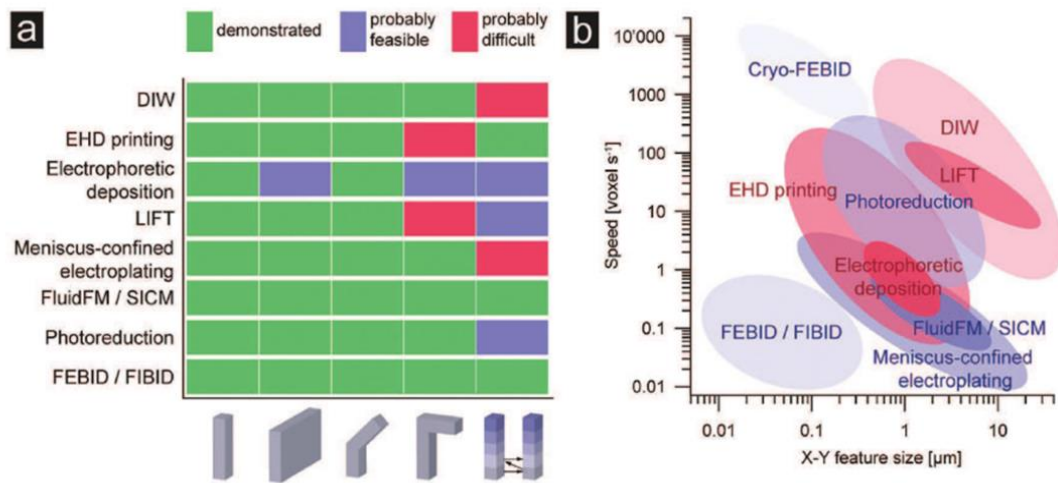


Figure 1-1 Capabilities and features of various metal micro/nano additive manufacturing technologies. a) A comparison of geometrical capabilities of each technique. b) Patterning speed versus x-y feature size of all techniques [19].

### **1.3 Objectives**

The main objectives of this thesis are:

1. To compare results from the recently developed predictive and control enhanced FEBID technique with experiments to further understand underlying deposition mechanisms.
2. To present multiple 3D FEBID data streams from experiments and simulations to bolster the case for investigating electron beam joule heating.
3. To use numerical and analytical methods to converge experimental and simulation results.
4. To utilize the insight on distortion causing mechanisms to further refine the FEBID simulation capability.
5. To apply dynamic feedback during deposition to update the exposure sequence toward defect free exposures or correct distortions in the initial design phase before deposition.

### **1.4 Outline of Work**

- Chapter 2 traces the evolution of focused electron beam induced deposition back to the early days when it was a process contaminant, up to the current developments in 3D nanoprinting.
- Chapter 3 presents the experiment and simulation set-up and discusses the rationale behind the selection of experimental and simulation parameters.

- Chapter 4 outlines the results from FEBID experiments and simulations both of which reveal defects in resulting nanostructures.
- Chapter 5 delves into analyzing the mechanism causing the defects and finally, a correction tool is introduced.

## **Chapter 2: Literature Review**

### **2.1 Development of Focused Electron Beam Induced Deposition**

Electron induced deposition was initially observed and reported in literature around 1913 [20]. A solid was formed on a surface where an electron beam intersected absorbed low-pressure gas at room temperature. Carbon contamination was also observed on surfaces when a carbonaceous gas was decomposed by electrons [21].

In the 1930s, when the first electron microscopes were built [22], carbon black particles attributed to electron induced contamination were observed as shown in Figure 2-1. This contamination was understood to be caused by the deposition of a hydrocarbon material under electron irradiation [23]. The mechanism of hydrocarbon formation on the substrate was the polymerization and condensation of organic vapors and gases, and certain other gaseous products, under electron bombardment. These contamination on surfaces originated from dirty metal surfaces, diffusion pump oil, rubber gaskets and hot vacuum grease which were common in the early SEMs [24].

By the early 1960s, contamination was no longer considered troublesome, but rather was viewed as a potential new area of research which led to micro patterning applications [25]. Christy then proposed a model describing the electron induced deposition of adsorbed molecules [26] that was summarized by Bret as shown in Figure 2-2 [27].

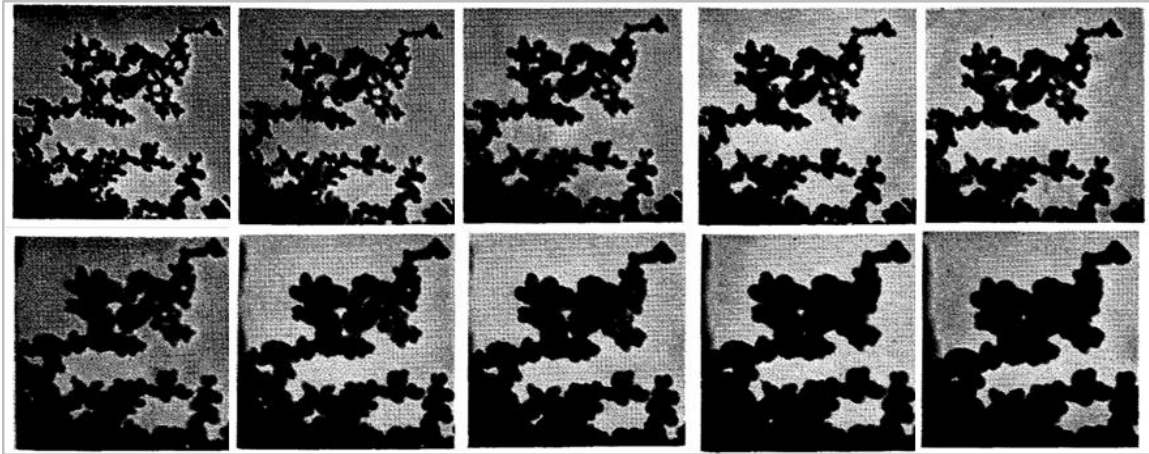


Figure 2-1 Shawinigan Acetylene Black under continuous electron collision in the electron microscope. Collision times (top left to bottom right) are: zero; 1 min.; 2 min.; 3 min.; 4 min.; 5 min.; 7 min.; 9 min.; 11 min.; 12 min. relative to the first exposure [15].

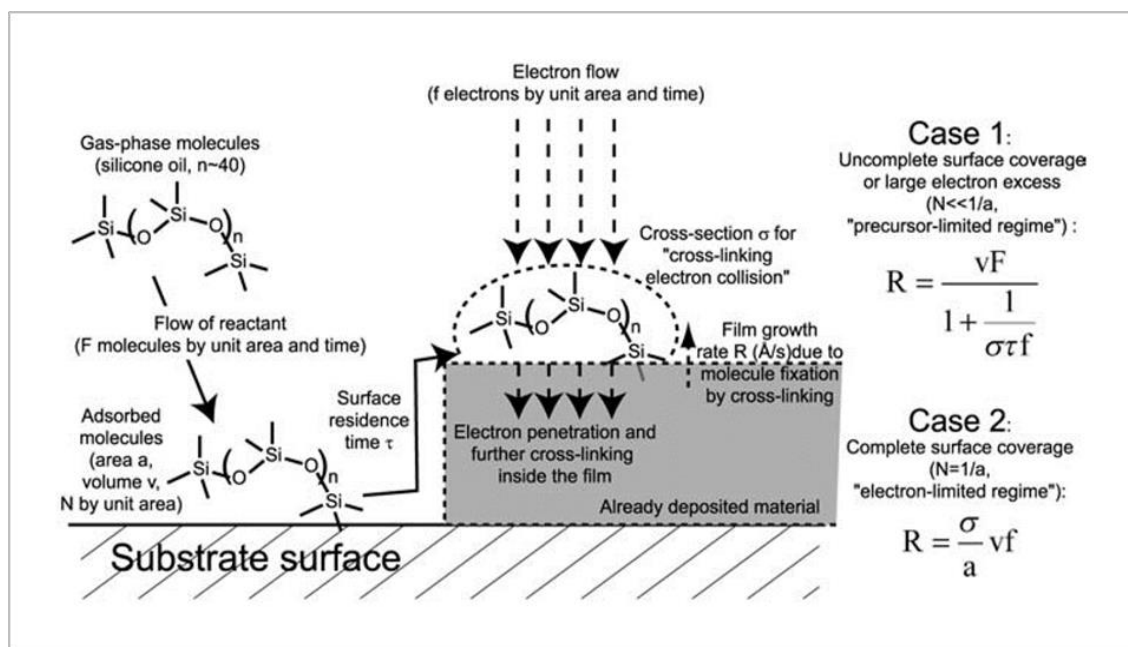


Figure 2-2 Christy's model of electron-beam-induced deposition.  $R$ : deposition rate.  $v$ : molecular volume.  $F$ : precursor flow.  $\sigma$ : cross-section of electron induced fixation.  $\tau$ : precursor residence time at the surface.  $f$ : electron flow.  $a$ : molecule.  $V$ : area.  $N$ : precursor surface density [18,19].

3D deposits were later formed by reducing the electron beam size of a stationary beam as shown in Figure 2-3 [28]. Tilted-view of the deposits revealed cone-shaped pillars which depended on how well the electron beam was focused (Figure 2-3) [29]. Lateral scanning of the beam deposited freestanding carbonaceous rods across a metallic edge (Figure 2-3) [30, 31]. The 3D contamination deposits were used in applications such as supertips for scanning probe microscopy [32], reference markers for AFM imaging [33], solder to join C nanotubes [34], and field emission tips [35]. The transition from troublesome contamination to 2D and 3D functional nanostructures was realized.

Organometallic precursors containing the desired chemical elements for functional deposits were then deliberately introduced in a SEM chamber and decomposed by an electron beam. For instance, in 1961, highly reflective superconducting Sn films were deposited from vapors of volatile tin derivatives ( $\text{Sn}(\text{CH}_3)_4$ ,  $\text{Sn}(\text{C}_4\text{H}_9)_4$ ,  $\text{SnCl}_2$ ) decomposed by electron beams with energies ranging from 50 eV to 1 keV [36].

Interest in focused electron beam induced deposition was renewed following new applications such as maskless high-resolution deposition in modified electron microscopes [37]. This new application involved heating the precursor reservoir and optimizing the gas supply which increased the growth rates and 3D structures were built in reasonable time frames [38, 39]. Then, with new CVD precursors came new focused electron beam induced chemistries and applications. For instance, Au deposits with 25-40% Au content were deposited from  $\text{Me}_2\text{Au}^{\text{III}}(\text{tfac})$  and were used as etch masks [40], X-ray absorbers [41], and supertips for scanning probe microscopy [42].

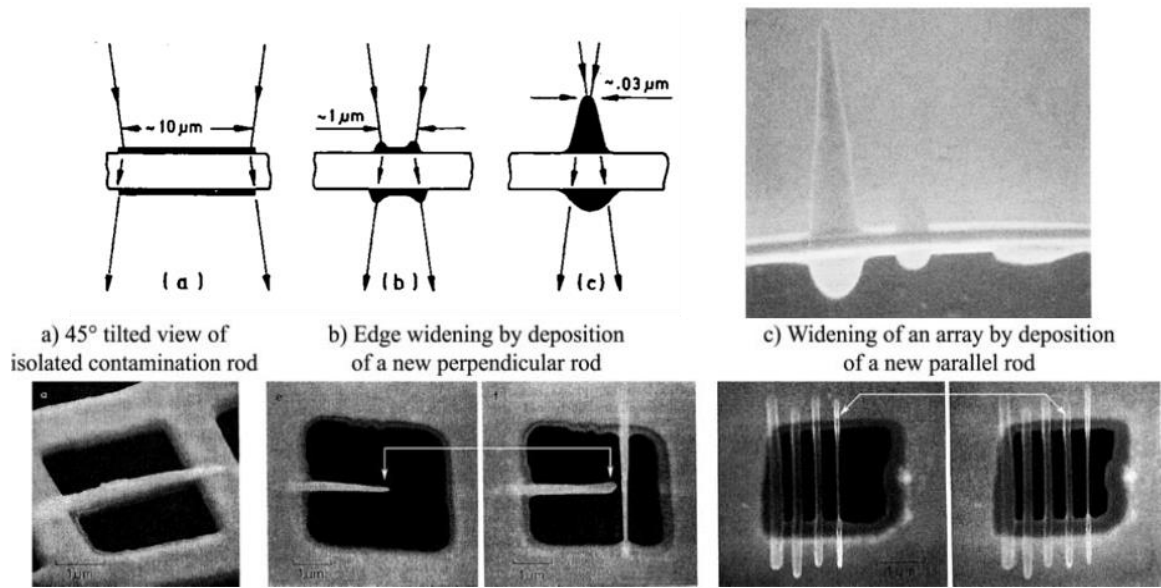


Figure 2-3 Illustration of 3D contaminant growth with decreasing beam size and contamination rods deposited by a lateral scanning beam [28-31].

Extensive studies on deposition mechanisms were done in the 1990s and several key discoveries were made: 1) The introduction of refresh time where the adsorbate is replenished by pulsing the beam was found to increase growth rate and paved the way for FEBID working reaction kinetics [43]. 2) The probability of adsorbate dissociation by secondary electrons was shown to exceed the dissociation caused by primary electrons. The energy transferred from secondary electron inelastic scattering events to the molecules disintegrates the adsorbed molecule. Residual energy from bond disruption is stored as vibrational energy which then serves as a recombinational energy of the non-volatile fragments formed during disintegration. The recombined fragments form stable compounds of metal nanocrystals and amorphous carbon matrix [44].

More recently in 2016, simulations of the focused electron beam induced deposition process were demonstrated and proven to be a powerful approach for the fabrication of complex 3D structures. Fowlkes et al. demonstrated that a simulation of the electron-solid interaction and the transient 3D spatial distribution of adsorbed precursor molecules can successfully predict the growth of 3D FEBID structures [17]. This made it possible to calculate dwell-times and beam coordinates prior to the experiment which enabled fabrication precision.

Figure 2-4 demonstrates prediction and control capabilities achieved by FEBID simulation, for example, Figure 2-4c shows a real  $\text{PtC}_x$  icosahedron and the geometry predicted by the simulation. Even more recently, Fowlkes et al. released 3BiD [45], a computer aided design program that enables quick and facile design of 3D-mesh objects for FEBID and generates exposure files that can be exported for direct use with an electron

microscope equipped with a gas-injection system. The implementation of a CAD program mostly eliminates trial and error and enables an accurate approach to FEBID. However, slight disparities between the prescribed design and the deposited structure have been observed.

Thus far FEBID has relied on precursors engineered for CVD, a high temperature process. When used in low temperature conditions such as FEBID, the deposits contain very high carbon content of 90 at. % and more for some precursors [46]. This often reduces or masks the intended function of the fabricated structure. However, there are some exceptions. CoFe alloy magnetic nanostructures were grown from the heteronuclear  $\text{HFeCo}_3(\text{CO})_{12}$  metal carbonyl precursor. The compositional analysis showed that the samples contained about 80 at% of metal and 10 at% of carbon and oxygen [47]. But where this is not the case, in-situ and post growth purification processes leading to pure and compact metallic nanostructure have been shown. Some examples of such processes are: fabrication on hot substrates [48], co-flow with reactive gases [49], synchronized laser assisted FEBID [50], and post growth scanning electron curing in the presence of  $\text{H}_2\text{O}$  vapor at room temperature [51].

The latter purification method was used in conjunction with the 3BID program to deposit free-standing, 3D plasmonically active nanostructures shown in Figure 2-5 [52]. The demonstration of predictable and controlled direct write of 3D functional nanostructures and the anticipation of specially designed precursors [53] shows that FEBID is the leading truly 3D nanoscale additive manufacturing technology.

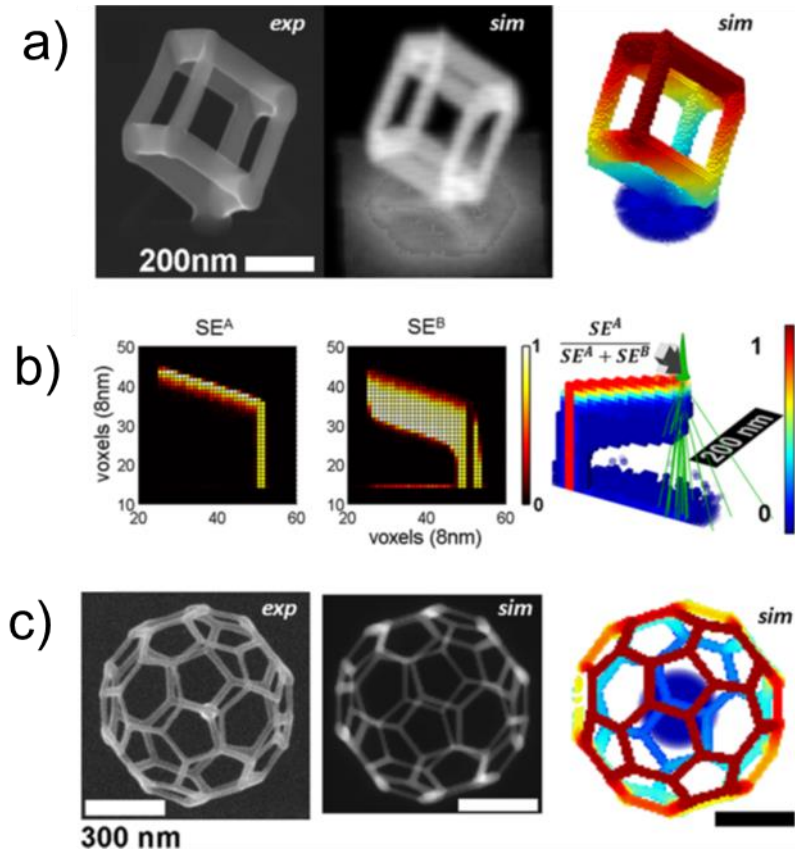


Figure 2-4 A demonstration of predictive and control capabilities of FEBID simulations. (a) and (c) compare electron micrograph images from experiments with virtual SEM images obtained from simulations. (b) Simulated secondary electron scattering events and morphology during 3D FEBID [37].

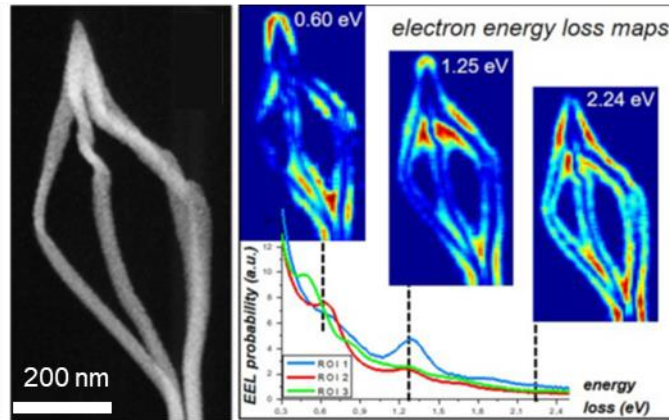


Figure 2-5 A deposited 3D plasmonic tetragonal bipyramid structure and its plasmonic response during electron energy loss spectroscopy measurements [45].

## 2.2 A Review of Electron Beam Induced Heating

When a collimated electron beam irradiates a target, inelastic electron interactions with the target atoms result in energy lost as heat in the irradiated material. This heat gives rise to a local temperature,  $T$  which is higher than the initial temperature  $T_0$ .

For electron energies above 100 keV, typical in transmission electron microscopes (TEM), the heating rate is given as:

$$\Delta Q = \Delta E \times \left(\frac{i}{e}\right) \times \left(\frac{h}{\lambda}\right) \text{ (eV/s)} \quad (2-1)$$

Where  $\Delta E$  is the average inelastic energy loss for each electron (eV),  $h$  is the thickness of the sample (nm),  $\lambda$  is the electron mean free path for inelastic scattering (nm),  $i_b$  is the electron beam current and  $e$  is the electron charge. At steady state, the heat generated is balanced by the heat loss through conduction since radiation in vacuum is negligible. Therefore,

$$\Delta E \times \left(\frac{i}{e}\right) \times \left(\frac{h}{\lambda}\right) = 4\pi k h \frac{T - T_0}{0.58 + 2 \ln\left(\frac{2R_0}{d}\right)} \quad (2-2)$$

where  $k$  is the thermal conductivity of the sample,  $R_0$  is the radial heat distribution from the irradiation spot, and  $d$  is the electron beam diameter [54].

To illustrate, Figure 2-6 shows the increase in temperature of various TEM samples as a function of electron beam current and thermal conductivity (W/m/K). The thermal conductivity indicated is not representative of all  $k$  in a class of materials. On one hand, high electron currents present significant beam heating effects, and this illuminates the

need, for example, of a condenser aperture to control the fraction of the electron beam allowed to hit the sample. On the other hand, low current densities also cause heating effects in insulating materials due to low  $k$ .

At relatively lower electron energies in SEM operations, typically in 5 – 30 keV range, the substrate is normally a bulk material. The heat flow is radial in three dimensions and leads to a smaller temperature rise compared to the TEM. In theory, when the beam size is much less than the electron range ( $R$ ), the temperature rise in a stationary beam is given by [55],

$$\Delta T = \left( \frac{1.5}{\pi} \right) \frac{i_b V_0}{kR} \quad (2-3)$$

where  $V_0$  is the acceleration voltage.

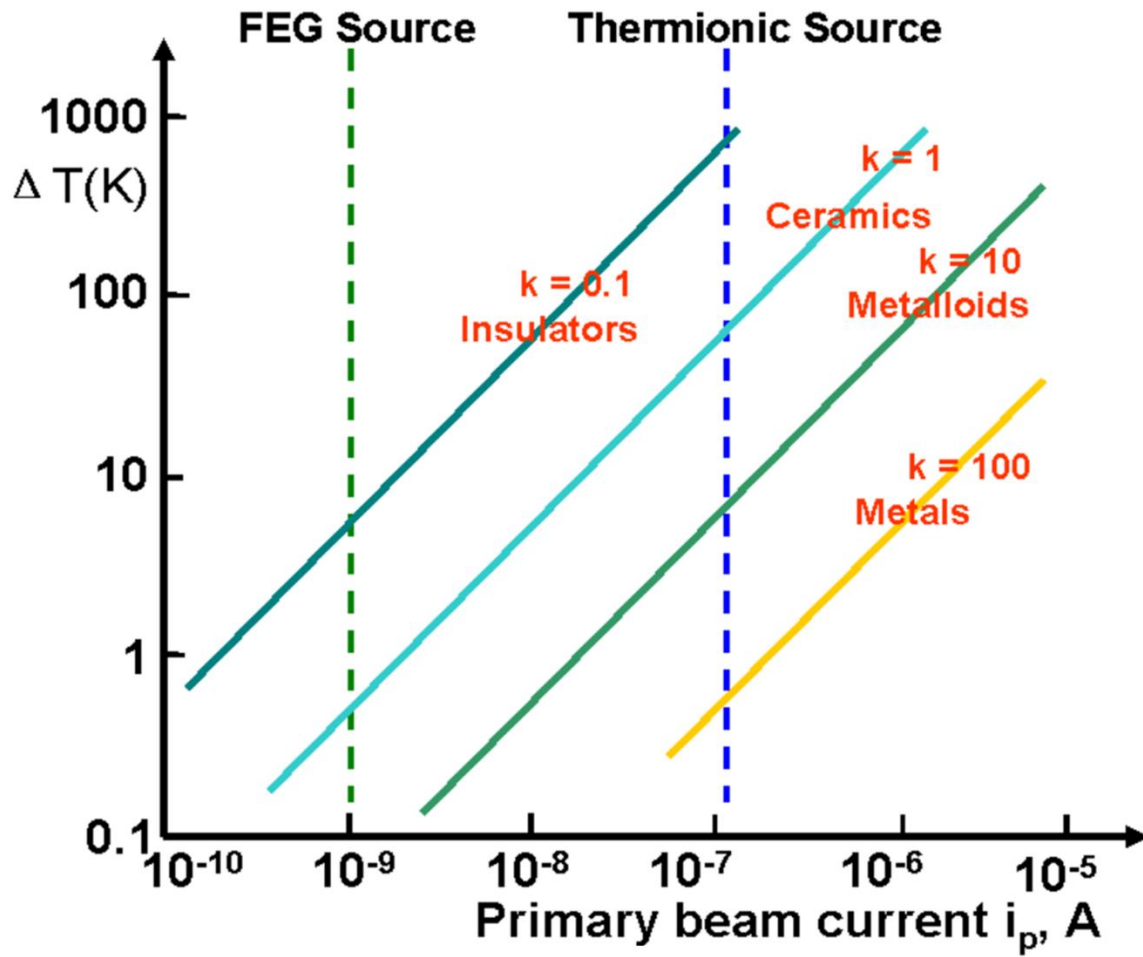


Figure 2-6 The increase of substrate temperature as a function of electron beam current and the thermal conductivity  $k$ , of the substrate [46].

### 2.2.1 Electron Scattering

When an electron transmits through a material the electron undergoes various elastic and inelastic scattering events as a result of interactions with the substrate material. The result of an inelastic scattering event is the loss of primary electron kinetic energy through plasmon and phonon excitations, secondary electron (SE) emission, x-ray generation and ionization. A significant fraction of this energy is dissipated as heat within the substrate material [56], causing a local temperature rise. Cumulatively, continuous electron energy loss decelerates an electron, which may eventually come to rest within in the material. Simultaneously, the electron undergoes a continuous trajectory redirection due to elastic scattering processes. Energy loss is not associated with elastic scattering. The combined influence of elastic and inelastic scattering events acts to confine the electron energy range of volume inside the substrate – in general, a tear-drop shaped volume often referred to the electron–solid interaction volume. The spatial range of this electron interaction volume is dependent on the primary electron acceleration voltage, and it is estimated by the Kanaya-Okayama electron range,  $R_E$  [16, 57]:

$$R_E = 2.76 \times 10^{-4} \frac{A(g/mol)E^{\frac{5}{3}}(eV)}{Z^{\frac{8}{9}}\rho(g/cm^3)} (nm) \quad (2-4)$$

where  $A$  is the atomic weight;  $E$  the incident electron energy;  $Z$  the atomic number;  $\rho$  the density. In bulk  $PtC_5$ , for instance, the electron range varies from 294 nm at 5 keV to 5820 nm at 30 keV, the typical FEBID primary electron energy range (Figure 2-7). Figure 2-7 reveals that the electron interaction volume is strongly dependent on the primary electron

energy. This physical dependence will be shown to have profound effects on the 3D nanoprinting process.

Elastic and inelastic scattering events both exhibit a marked energy dependence. In 1930, Bethe proposed an analytical model to the total electron energy loss, by all possible inelastic mechanisms, that is still in use today. Later Joy and Luo modified the expression because as the energy (E) falls, some inelastic events become inaccessible. The rate of energy loss per scattering event,  $dE/ds$ , can be determined by the Joy-Luo [58] modification of the Bethe-loss relation [59] for energies ranging from 50 eV to 100 keV, given as,

$$\frac{dE}{ds} = 78500 \frac{\rho Z}{AE} \ln \left( \frac{1.166E}{J} + 1 \right) \quad \left( \frac{keV}{cm} \right) \quad (2-5)$$

where J is the average rate of inelastic energy transfer, that is, the mean ionization potential. J can be calculated by the expression:

$$J = \left[ 9.76 Z + \frac{58.5}{Z^{0.19}} \right] \times 10^{-3} \quad (keV) \quad (2-6)$$

As mentioned above, a significant portion of the inelastic energy loss resulting in Joule heating of the substrate. Joule heating is the process by which an electric current is converted into heat as it flows through a resistance. If heating is expected to influence the FEBID 3D nanoprinting process, then a mathematical treatment to predict heat flow in solids is required which is the differential heat equation.

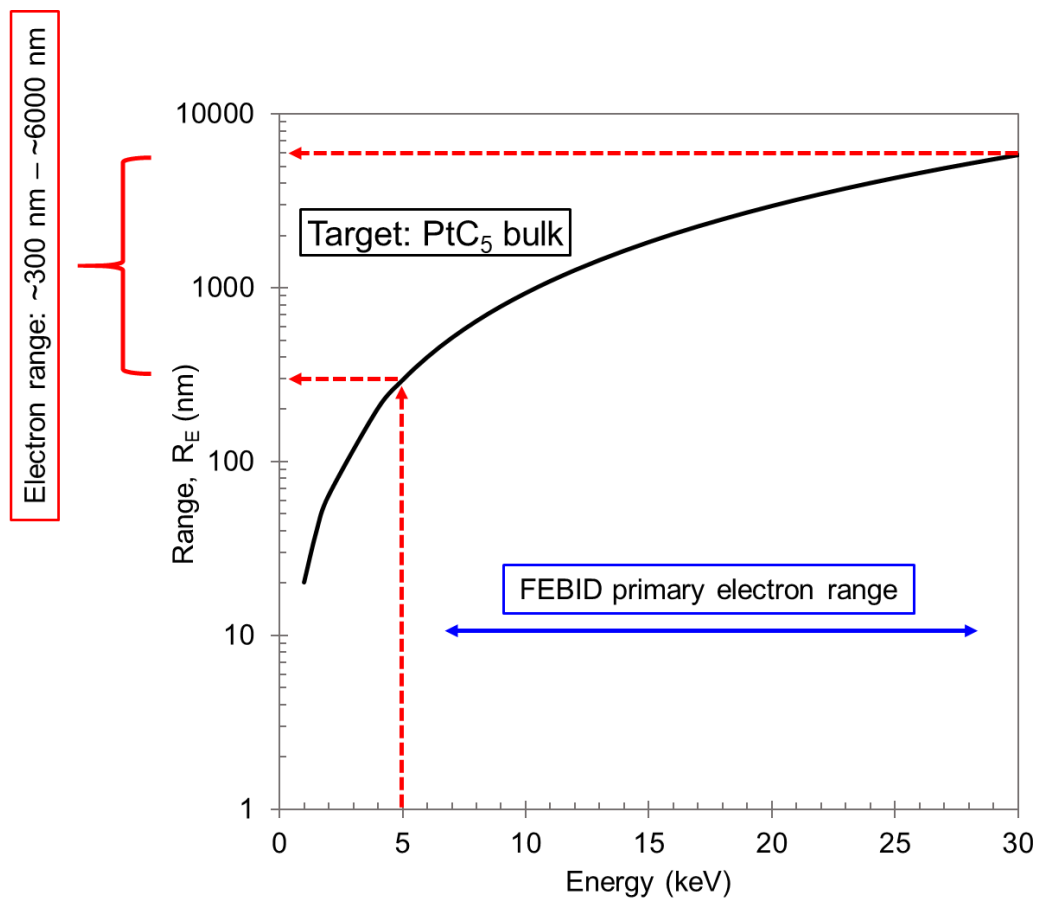


Figure 2-7 Electron range in bulk PtC<sub>5</sub> estimated using the Kanaya–Okayama formula (Equation 2-4) for the typical FEBID primary electron energy range.

### 2.2.2 Electron Beam Induced Heating

Under the steady state heat transfer condition, the heating rate caused by the electron beam ( $q_{in}$ ) is equal to the heating rate dissipated within the material ( $q_{out}$ ). The steady-state condition in three-dimensional cylindrical coordinates can be defined as:

$$k \left( \frac{\partial^2 T}{\partial r^2} + \left( \frac{1}{r} \right) \frac{\partial T}{\partial r} + \frac{\partial^2 T}{\partial z^2} \right) + H(r, z) = 0 \quad (2-7)$$

where  $k$  is the thermal conductivity,  $T$  is the temperature,  $r$  is the radial coordinate,  $z$  is the axial coordinate, and  $H(r, z)$  is the heat source expression for a stationary electron beam [16, 56].

During 3D FEBID, the electron beam is held for relatively long periods in stationary mode (characteristic time =  $10^{-3}$  s), in between brief, digital translations (characteristic time  $\ll 10^3$  ms). In beam translation, the beam is off, and the deposit momentarily cools. However, as will be shown later, steady-state conditions are quickly reestablished and the problem may be treated, without a loss of accuracy, under steady-state heating conditions.

Also, the heat and dissipation thereof are dependent on geometry. In the past, the temperature rise within semi-infinite geometries, thin films, and 3D FEBID nanostructures have been estimated using analytical methods and Monte Carlo simulations.

### 2.2.3 Semi-Infinite Substrate Geometry

The maximum temperature rise  $\Delta T$ , relative to the bulk substrate temperature, within the electron interaction volume on a bulk substrate can be analyzed by assuming that the heat generated by the incident electron beam dissipates uniformly within a hemisphere whose radius is half the electron range,  $R_E/2$  [16]. The heat dissipates through conduction in the three spatial coordinates within the bulk substrate, and is estimated as [60]:

$$\Delta T_{bulk} = \frac{E_o i_b (1 - \eta)}{(\pi k R_E)} \quad (2-8)$$

where  $i_b$  is the primary electron current,  $\eta$  is the backscattered electron yield, and  $k$  is the thermal conductivity of the substrate.

Chu et al. demonstrated direct temperature measurements on a bulk substrate using nano-thermocouples [61]. They fabricated 400 nm Au/Ni thermocouples and used them to measure the temperature at the contact surface between a 300 nm PMMA layer and a 1  $\mu\text{m}$  SiO<sub>2</sub> layer. Irradiation by a 15 keV, 600 nA electron beam current with a 2  $\mu\text{m}$  beam radius resulted in a 70 K temperature increase. The temperature increase reached a steady state in 10  $\mu\text{s}$ .

#### 2.2.4 Thin-Film Geometry

The temperature increase in suspended thin films, with no underlying substrate can be evaluated as [62],

$$\Delta T_m = \left( \frac{dE}{ds} \Delta s \frac{i_b}{e_0} \right) \frac{\ln(2r_m/r_B)}{2\pi\kappa_m t_m} \quad (2-9)$$

where  $r_B$  is the electron beam radius and  $r_m$  is the heat sink radius. Thin films, particularly TEM membranes, typically have a thickness of about 10 nm. Electrons with energies less than 1 keV transmit through the membranes, and the membrane thickness defines the average electron trajectory path,  $\Delta s = t_m$ . In this case, heat dissipates in two dimensions with insulating boundaries forcing a constant temperature in the relatively thin, thickness coordinate. However, another dimension where the heat dissipates can be added by depositing 3D nanostructures on thin films [56]. The 3D features increase the average electron trajectory to the  $z$  length of the nanostructures and  $\Delta s = L_{\text{dep}}$ . Utke et al. stated that “since the heat dissipation in membranes is reduced to two dimensions, the temperature increase in pillars on membranes becomes more important than on bulk substrates.” [16] However, in this dissertation, we will show that temperature increase in pillars on bulk substrates is substantial and leads to loss of structural integrity of deposited 3D nanostructures.

### 2.2.5 3D FEBID Nanostructures

Localized temperature increase  $\Delta T$  at the tip of a vertical pillar with height  $L_p$ , radius  $r_p$ , and heat conductivity  $k_p$  is given by [62]

$$\Delta T_p = \left( \frac{dE}{ds} \Delta s \frac{i_b}{e_0} \right) \frac{16L_p}{\pi k_p r_p^2} \quad (2-10)$$

It is assumed that heat generated at the pillar tip is dissipated through conduction down the height of the pillar to the heat sink. This assumption holds because heat loss through convection and radiation in a vacuum environment can be neglected [56]. Since the heat generated is localized in the irradiated tip, the thermal conductivity of the pillar drives the steady-state temperature of the pillar. Therefore, the thermal conductivity of a bulk substrate has little to no effect on the apex temperature.

For a given energy, Equation 2-7 can be revised and written as  $\Delta T_p = C_1 \Delta s L_p$ . That is, if the pillar height is smaller than the penetration range of the incident electrons, a fraction of the primary electrons will penetrate the substrate. The average electron path in the pillar becomes  $\Delta s \sim L_p$ , therefore,  $\Delta T_p \approx C_1 L_p^2$ . This square relationship agrees with Monte Carlo and finite element simulations by Randolph et al. [56], as shown in Figure 2-7a. This Figure shows that as the pillar height increases, the temperature at the tip increases, and the increase is at a higher rate. This rapid rise in temperature provides insight into the effects of electron beam induced heating. A temperature-dependent property, such as precursor mean stay time, decreases with an increase in temperature. Thus, the precursor molecule surface count is reduced, resulting in a slower growth rate for tall pillars (Figure 2-7b).

In general, lower primary electron energies have a smaller interaction volume. Therefore, the heat generated by lower energy beams is concentrated at the tip of the pillar resulting in higher pillar temperatures. For nanowires grown by lateral scanning of the beam (segments), the energy loss pathlength is defined by thickness in the z-direction,  $b_z$ . Pure metal nanowires exhibit negligible temperature rise [63]. Typically, however, most of the FEB deposits consist of metallic nanocrystals embedded in a carbon matrix with low heat conductance. Nonetheless, thermal decomposition by electron beam induced heating has been shown, where high metal-content structures were deposited for  $\text{Co}_2(\text{CO})_8$  [64] and (hfa)Cu-TMVS [65]. In the case of the Cu precursor (Figure 2-8), an electron-beam deposited 3D vertical pillars and horizontal segments. The segments comprised of 2 - 5 nm Cu crystals in an amorphous carbon matrix. These segments were then used as support structures for the pillars. The pillars consisted of coalesced 100 nm Cu crystals. These high Cu-content pillars grew at a rate of 5 - 6 nm/s in contrast to Cu pillars deposited on a bulk substrate at an elevated rate of 23 nm/s. This increase in growth rate further validates the substrate geometry dependence of electron beam induced heating. Heat transfers rapidly through bulk substrates versus through FEB deposits and thin films, hence the higher growth rate on bulk substrates.

A significant drawback with FEB deposited material remains. The thermal conductivity of most FEB deposits, typically comprised of carbon-metal nanocomposites, is unknown. It can range between 0.01 W/m/K for polymers to 400 W/m/K for metals. Further, for the temperature to be of import, successive electron impingements need to be shorter than  $10^{-10}$  to  $10^{-11}$  s [60], the electron-phonon relaxation time. Electron succession time is calculated as  $e^-/I_p$ ; therefore, it takes 0.1 ns for a beam current of 2 nA.

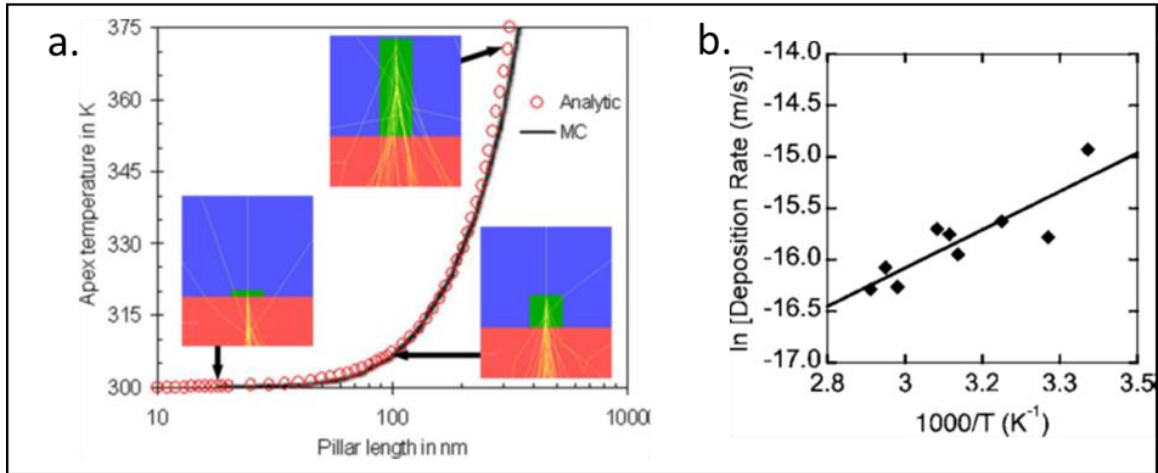


Figure 2-8 (a) Comparison of simulations with analytical estimation given by Equation 2-7. A  $\text{SiO}_2$  pillar with 100 nm diameter irradiated by a 20 keV, 500 pA beam. Inset: 30 electron trajectories at pillar lengths of 20, 100, and 300 nm showing the shift of the interaction volume from the substrate into the pillar. (b) Arrhenius plot of the  $\text{SiO}_2$  deposition rate as a function of temperature. Deposition rate decreases with increase in temperature [47,56].

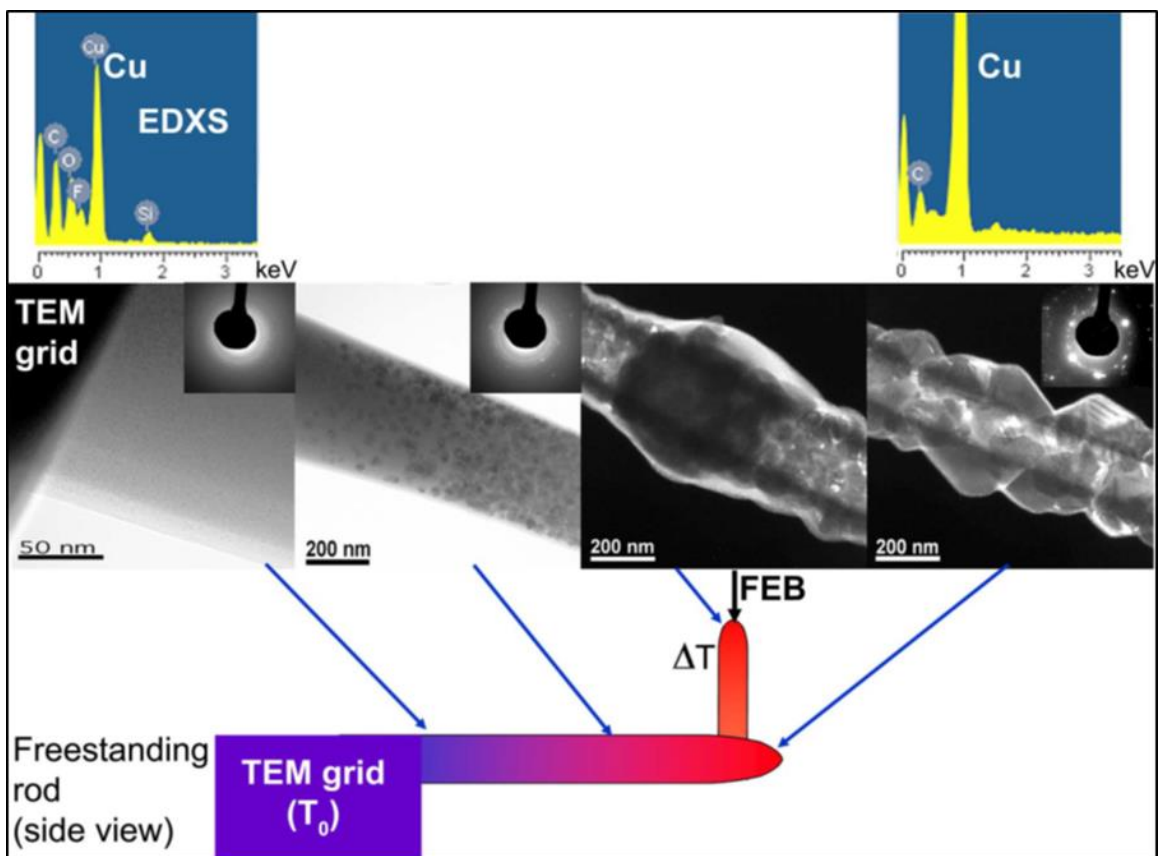


Figure 2-9 Effects of temperature rise on FEBID nanostructures. Morphology and composition change due to a temperature gradient along a horizontal freestanding nanorod. EDXS indicates increasing Cu metal content in the deposits, with increasing crystal size [49,57].

### **Chapter 3: Materials and Methods**

3D Nanostructure patterns generated by 3BiD [45] - a computer-aided design program for micro/nanoscale focused beam induced deposits - were deposited in a Thermo Fisher Scientific NOVA 600 dual-beam (electron and  $\text{Ga}^+$ ) instrument fitted with a gas injection system (GIS). Only the electron beam was used to perform these experiments. The electron beam parameters and GIS set up used for the experiments are described in Section 3.1. During the deposition, real-time sample current data was collected using a Keithley (A Tektroniks Company) Model 6485 picoammeter attached to the dual-beam stage. This characterization method is detailed in Section 3.2. Additionally, coinciding FEBID simulations [17] were done for a better understanding of the growth mechanics during 3D deposition and to extract some material properties. A brief review of the patterning software and the concurrent simulations is discussed in Section 3.3.

### **3.1 Electron Beam Parameters**

#### **3.1.1 Beam Acceleration Energy and Beam Current**

Precision in the deposition process for growing freestanding 3D mesh nanostructures is crucial since the structural integrity of the whole depends on the individual elements. Therefore, growth dynamics must be considered to achieve precision and repeatability. In general, how much material is deposited under given conditions is of most practical interest.

The balance between precursor molecules and dissociating electrons within the region of interest dictates the deposition rate and resolution of the 3D structures. This precursor-electron balance is distinguished into three essential process kinetics [18, 66]:

1. Precursor-limited, where there is a large number of irradiating electrons and, surface diffusion is negligible. The maximum deposition rate is determined by the replenishment of precursor gas directly from the GIS. Hence, the precursor adsorption from the gas phase limits the deposition rate.
2. Diffusion-enhanced is where precursor refreshment occurs predominantly by surface diffusion as opposed to gas-phase replenishment. Diffusion-enhanced is an intermediary stage between precursor-limited and electron-limited reaction domains.
3. Electron-limited is characterized by a fast precursor refresh rate compared to the rate at which electrons dissociate the precursor molecule.

The deposition rate and resolution are vital factors when considering the electron beam parameters to use for 3D nanoprinting using electron beam deposition. High deposition rates and resolution are desirable and are achieved when the precursor is continuously replenished by surface diffusion, and depletion is avoided. That is to say, the electron-limited reaction is established, and the deposit retains the shape of the electron distribution. Therefore, the smaller the electron probe size, the better precursor refreshment can be achieved by surface diffusion, and the higher the resolution [16, 66].

In current systems, modulating electron flux is facile in comparison to controlling the amount of precursor gas delivered to the system. Electron beam energies ranging from 2 keV - 30 keV, and beam currents in the single-digit picoamps (pA) to hundreds of nanoamps (nA) range are readily accessible in the NOVA 600. However, to deposit highly resolved 3D nanostructures with high efficiency, electron-limited conditions must be maintained during the experiments. These conditions are achieved by using low beam currents and high beam energies.

A FEBID parameter study by Winkler et al.[18], shows the growth effects of various beam currents and beam energies. They found that higher beam currents formed deposit artifacts, such as co-deposits and side-branches as shown in Figure 3-1. They also observed stagnated growth on structures deposited using the higher beam currents, which is indicative of precursor-limited conditions. The lowest beam currents, however, generated the most accurate nanostructure shapes.

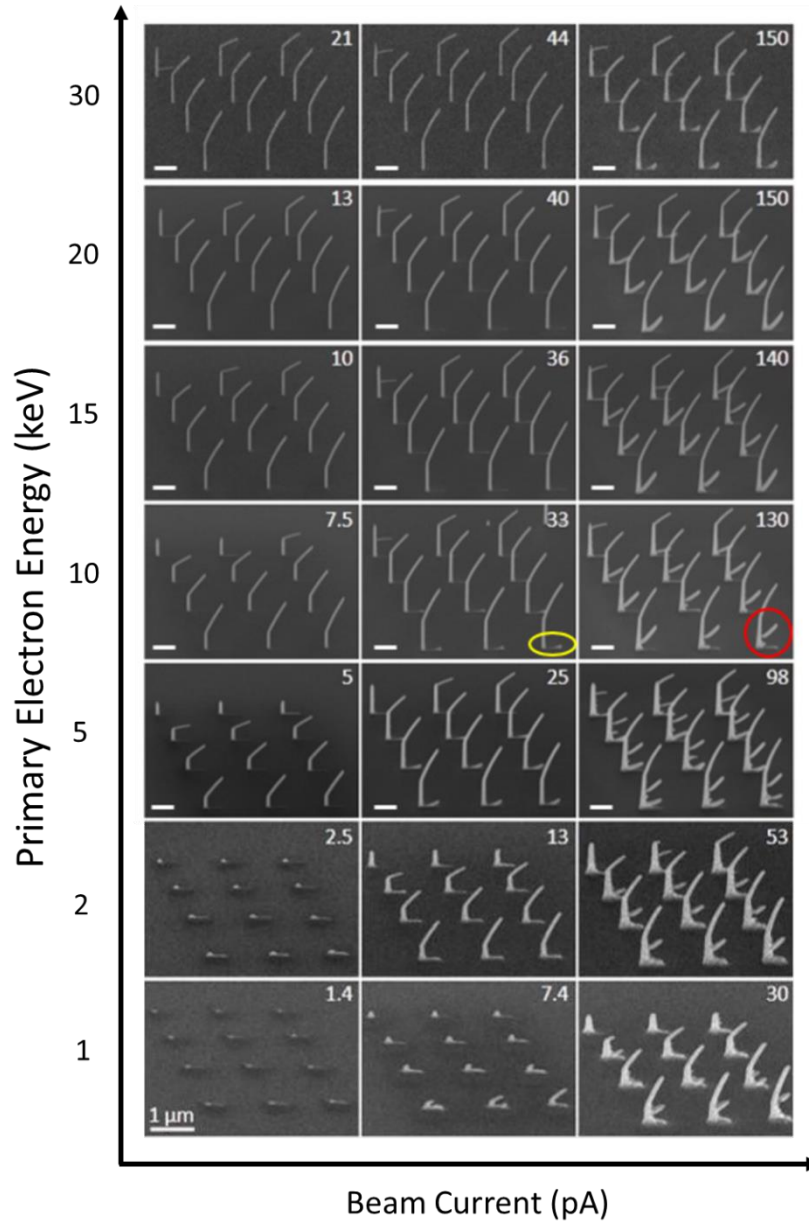


Figure 3-1 Tilted SEM images of calibration structure arrays deposited at different primary electron energies and currents (indicated on image top right). Co-deposits and co-branches marked by yellow and red circles, respectively [59].

Contrarily, the highest beam energies exhibit more resolved nanostructures, even though they lag in growth efficiency. This result from higher beam energies is because they have:

1. A smaller substrate interaction volume which leads to a lower areal density of backscattered electrons ( $\eta$ ) and secondary electrons emitted by the backscattered electrons ( $\delta_{II}\eta$ ). Hence limiting growth artifacts [67].
2. Following that, a smaller dissociation cross-section which results in reduced dissociation efficiency — in essence, leading to a higher number of precursor molecules still available for dissociation (electron-limited conditions) [16].

For these reasons, all the experiments were conducted using a 30 keV electron beam acceleration energy set on the instrument at 21 pA beam current, unless otherwise mentioned. This beam energy is the highest attainable in the dual-beam, and the beam current is the lowest setting at that energy. Importantly, the structures were deposited on bulk Si substrates with 5 nm SiO<sub>2</sub> thin film on the surface of the substrate.

### **3.1.2 Beam Focus**

The precision of electron beam focus strongly impacts both the deposition rate and deposit spatial resolution. The minimum beam size for a given combination of primary electron beam energy and current yields faster deposition rates and, in general, produces the highest resolution nanostructures compared to a defocused electron beam. Ultimately, the beam current density has implications on influencing precursor dissociation and replenishment working conditions. When the beam is finely focused, precursor is more

rapidly consumed and a surface concentration gradient around the beam impact region is established. The emergence of the gradient in precursor surface concentration, or coverage, inherently indicates that replenishment from the vapor phase is inadequate to fully restore the equilibrium surface concentration – the concentration of precursor present on the surface when the primary electron beam is off. It has already been established that 3D nanoprinting using EBID occurs under the precursor-limited reaction regime where deposition is inefficient and surface concentration gradients maintain growth [18, 67]. Thus, in the experiments reported here, deposition occurs at average surface precursor concentrations less than the equilibrium value, yet the highest vertical deposition rates are achieved with the most resolved electron probe possible. This regime is consistent with that reported by Plank et al. [68] where it was found that a larger beam size (defocus) produces a lower vertical growth rate. The resulting 3D nanostructures deposited by a stationary beam broadened and decreased in height as the beam defocus increased (Figure 3-2). In another observation [18], nanostructures deposited in the limit of a relatively large defocus, using a moving electron beam, failed.

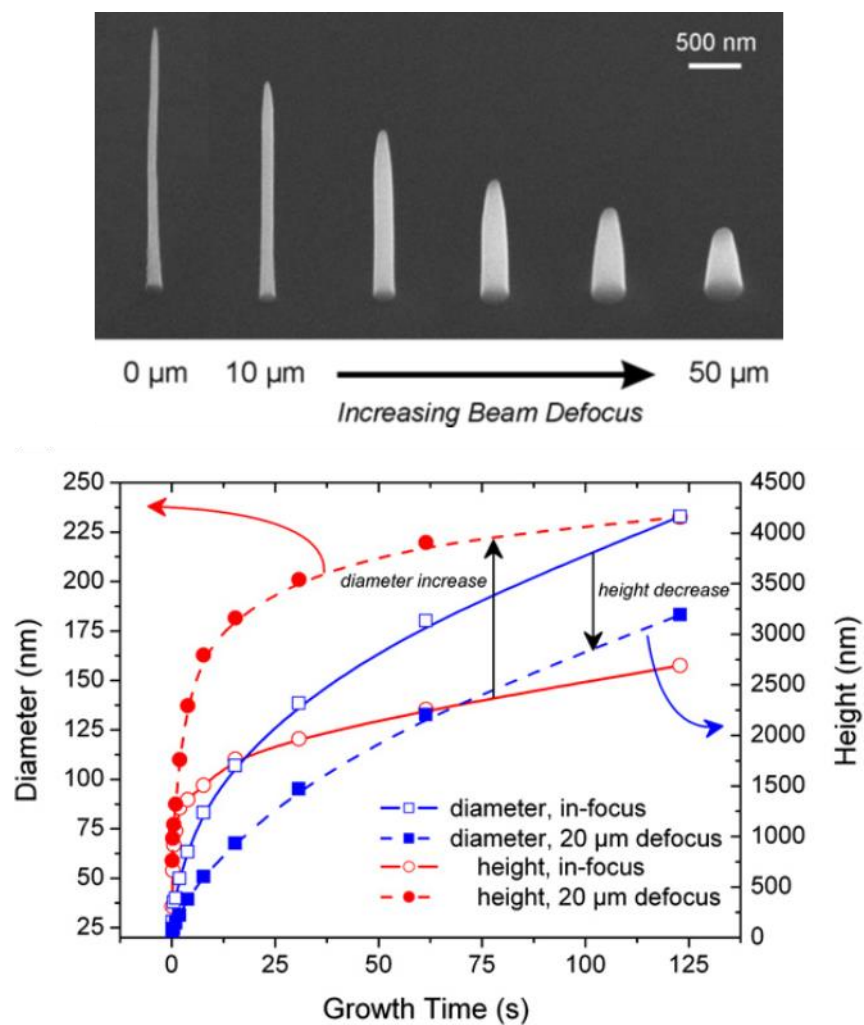


Figure 3-2 Top: Tilted SEM images of vertical pillars showing electron beam defocus effects. Beam defocus is increased from left to right. Bottom: The evolution of Pt pillar diameters (circles) and heights (squares) for focused (open symbols) and 20  $\mu\text{m}$  defocus (filled symbols) conditions. Experimental conditions: 30 keV, 150 pA, 4 ms dwell time, 28 ms refresh time [61].

### 3.1.3 Gas Injection System

A gas injection system (GIS) delivers a highly localized precursor flux to the electron beam impact region on the substrate such that practical deposition rates can be achieved (order of seconds/minutes) while maintaining a low chamber pressure for electron beam operation; if the precursor vapor pressure becomes too large the vapor phase will scatter the electron beam in transit to the substrate thereby degrading the electron probe lateral resolution at impact. Although injected to a position within micrometers of the beam impact region, at least two degrees of freedom remain to position the substrate underneath the gas injection needle. Proper GIS alignment is essential because it determines the deposition working condition; that is, the deposition rate and resolution - which rely on whether the process is precursor-limited or electron-limited - are driven by how efficiently precursor molecules are replenished soon after dissociation. A strongly directed precursor flux generates shadow artifacts on high aspect-ratio nanostructures, which obscures the incoming precursor flux resulting in decreased deposition rates [69]. Fowlkes et al. [17], however, demonstrated through simulations that high surface coverage by a diffuse flux minimizes deposition rate variations. This type of coverage is achieved by aligning the GIS needle close to the substrate surface. The near-substrate GIS alignment also ensures that lateral gradients that could be imposed by isoflux contours of the impinging precursor molecules are avoided.[69-72].

### 3.1.4 Electron Beam and GIS Experiment Set-up

All experiments were conducted in a Thermo Fisher Scientific Nova600™ dual beam system equipped with a gas-injection system. Trimethyl(methylcyclopentadienyl)platinum(IV) ( $\text{MeCpPt}^{\text{IV}}\text{Me}_3$ ), a commonly used organometallic precursor for platinum (Pt), was introduced into the chamber via the gas injection system. The Pt precursor melts at  $30^\circ - 31^\circ \text{C}$ . It was preheated to  $45^\circ \text{C}$  for 30 min before the deposition to ensure that a continuous and stable gas flux was delivered to the beam impact region. The final composition of the deposits is assumed to be  $\text{PtC}_5$  which overestimates the deposit purity based on reported experiments carried out on different, yet complementary, geometries such as films and pillars ( $\text{PtC}_6$  and  $\text{PtC}_8$ ) [73, 74] and the composition  $\text{PtC}_5$ , [17, 45] suggested by simulations, that best emulates experiments

A commercial Thermo Fisher Scientific-GIS was used for these experiments. The GIS components are shown in Figure 3-3. The GIS needle is retracted and inserted via a pneumatic actuator controlled electromechanically from the microscope user interface. The inserted position was aligned at a  $52^\circ$  incidence angle relative to the substrate. The base of the needle was positioned at 100  $\mu\text{m}$  vertical distance above the substrate, 25  $\mu\text{m}$  and 28  $\mu\text{m}$  in the x- and y-direction from the center of the electron beam, respectively at  $\sim 5 \text{ mm}$  focal working distance. The electron beam center is perpendicular to the substrate at no tilt (view normal to the page of the electron micrograph in Figure 3-3). The substrate was cleaved from new Si wafers (with a 5 nm native  $\text{SiO}_2$  layer) in a cleanroom setting. The Si chip was adhered to a metallic sample holder using conductive copper tape as

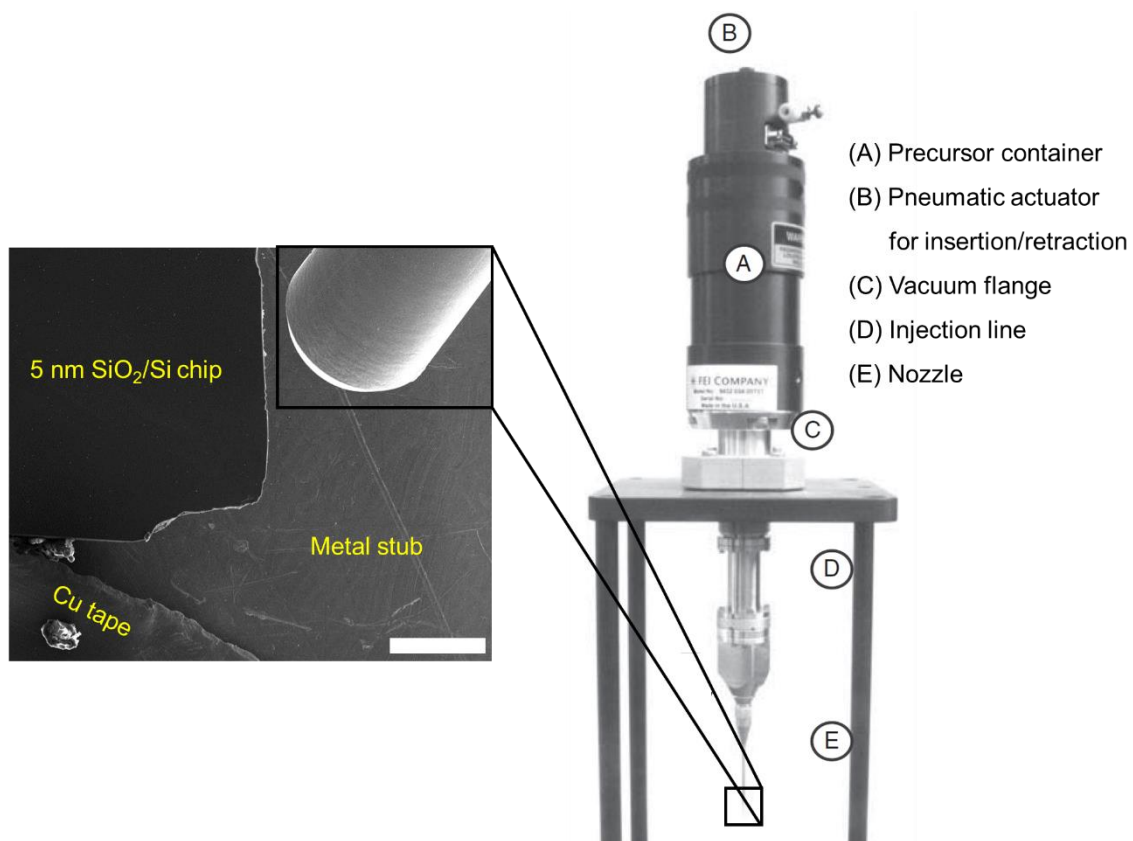


Figure 3-3 3D FEBID experimental set up. Thermo Fisher Scientific Gas injection system components and an electron micrograph of the GIS nozzle on 'insert' position inside the Nova600™ dual beam system. Scale bar = 0.5 mm.

indicated in Figure 3-3 to mitigate drift and sample charging, then immediately loaded to the microscope chamber.

After loading the sample, and once the standard operating chamber pressure of  $1 \times 10^{-6}$  mbar was reached, the stage was moved to the desired working distance (100  $\mu\text{m}$  from the base of the GIS needle), and initial beam focus and astigmatism corrections were done. To further refine the electron beam focus, small pillars were deposited at high magnification (300kX) near the region of interest until pillar diameters below 50 nm were achieved in top view. The focus pillars were deposited using single-pixel dots on a bitmap pattern at 1 ms dwell and 1000 passes.

Immediately before depositing the focus pillars, the needle was inserted, then the GIS valve was opened for at least 2 min to allow quasi-steady-state precursor coverage on the substrate. The electron beam was blanked while the valve was opened. Background chamber pressure was used to monitor when the temporary equilibrium was reached. Once the GIS valve was opened and the precursor gas was introduced into the chamber, there was an initial burst in chamber pressure, followed by a steady increase, and finally, the pressure stabilized at  $2 \times 10^{-5}$  mbar. Beam focus was optimized near the area of deposition (approximately 5  $\mu\text{m}$ ) to sustain the beam focus. This procedure was followed before depositing desired 3D nanostructures for all experiments.

After deposition, the nanostructures were analyzed by scanning electron imaging at 52° stage tilt. Before the analysis, the beam was blanked, the GIS valve closed, and the needle retracted to avoid any needle distortions. An additional 10 min wait was applied to

encourage desorption of precursor molecules so that additional undesired deposition and nanostructure broadening was avoided. Further electron exposure of the deposits was reduced by imaging at low doses.

### **3.2 Sample Current Collection**

*In situ* substrate currents were collected during 3D FEBID using a Keithley Model 6485 Picoammeter (Figure 3-4) that was externally connected to the microscope stage. The acquisition rate of the picoammeter during the FEBID experiments is 17 data points/s. Sample current collection was initiated by toggling the picoammeter on at the instant the electron beam is unblanked, and toggle off post deposition.

### **3.3 FEBID Computer Aided Design Program (3BiD)**

The 3BiD [45] program features a pattern generating graphical user interface (Figure 3-5) where mesh style 3D nanostructures are designed. Once the design is complete, it is exported as a stream file that contains a list of X and Y co-ordinates plus the beam exposure duration for each co-ordinate. Accurate design replication during deposition is dictated by how well the CAD program is calibrated to the electron microscope operating conditions. Calibration entails adjusting for both the stationary and scanning electron beam modes. For the stationary mode, a pillar is deposited with a primary electron beam fixed at a point (x,y) in the focal plane. The total length of the pillar is used to calculate the average vertical growth rate, an input parameter required by the CAD program. For the beam scanning mode, a nanowire is deposited with its projected length parallel to the focal plane, referred to here as a segment. The characteristic parameter of a segment is the angle ( $\zeta$ ). An array of segments of varying angles, ranging from  $0 \rightarrow 90^\circ$ ,

deposited on supporting pillars are used to derive a calibration curve (Figure 3-5). The calibration curve converts the CAD into an FEBID exposure file. During the calibration, a segment angle ( $\zeta$ ) versus the segment dwell time ( $\tau_d$ ) plot is generated for the full range of ( $\zeta$ ). This plot is uploaded to the CAD program. Later, once a design is created, the program determines the required dwell time ( $\tau_d$ ) for each defined ( $\zeta$ ) from the calibration curve.

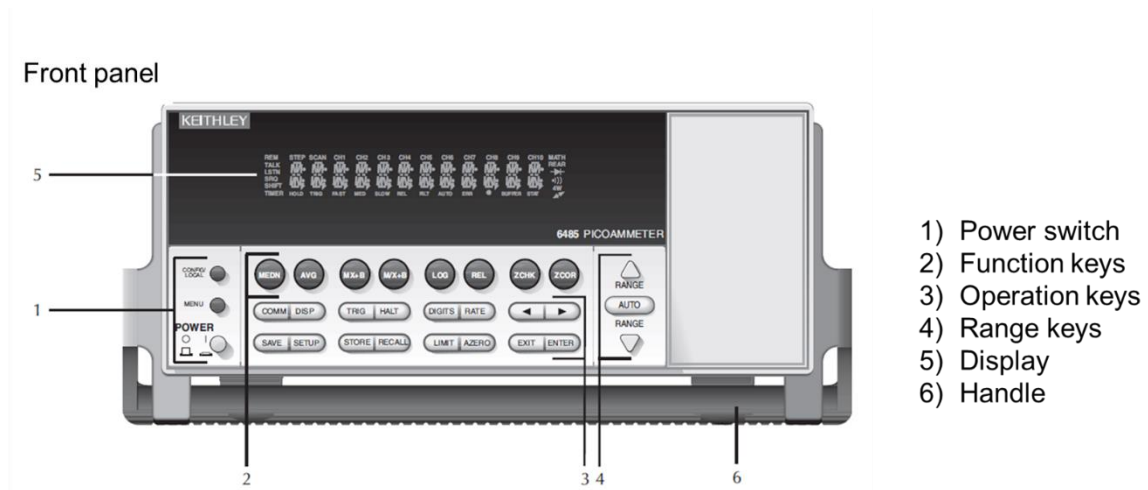


Figure 3-4 The front panel of a Keithley Model 6485 Picoammeter used to collect sample current during FEBID.

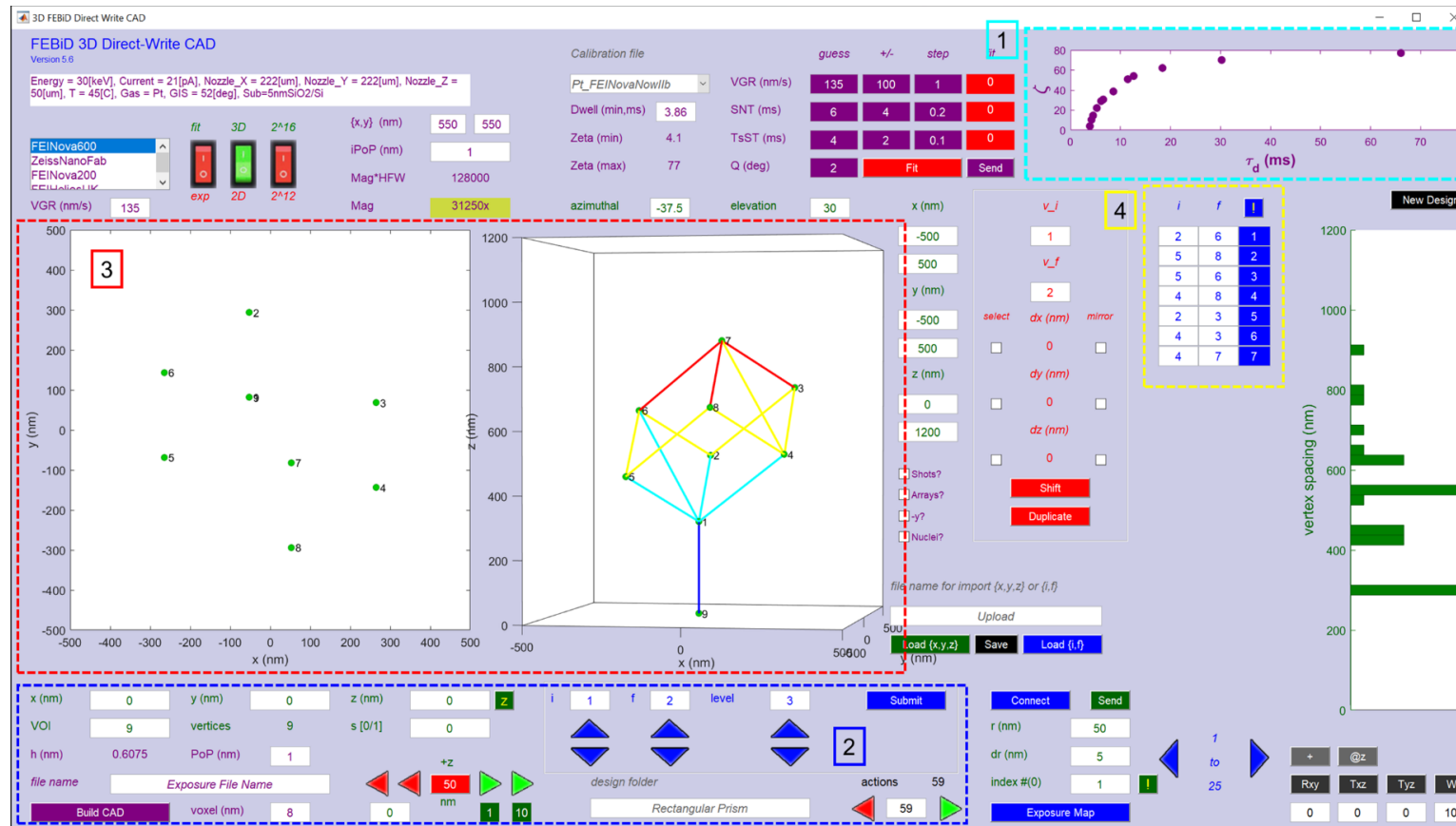


Figure 3-5 3BiD [38] CAD Graphical user interface for 3D FEBID design and exposure file generation. The features highlighted are (1) the  $\zeta$  vs  $\tau_d$  calibration file, (2) vertices and vertex-vertex interconnects assignment tabs, (3) 2D and 3D design view panels, and (4) exposure level sequence toggle panel.

## Chapter 4: Results

### 4.1 Single Calibration Structure

A calibration structure, the most basic geometric element required to deposit any 3D mesh style object, consists of two connected nanowires termed pillar and segment exposure elements. The pillar element is a vertical nanowire that serves as a support for the segment element (Figure 4.1). The pillar is deposited using prolonged and stationary electron beam exposure. The segment is deposited, starting at the pillar apex, using lateral translation of the electron beam moving in the x, y direction, i.e., the substrate plane, at a constant digital speed. Specifically, the speed is equal to the pixel point pitch divided by the dwell time per pixel. A transition stage of deposition is observed, between pillar and segment deposition, during which the beam irradiates the underlying pillar during initial segment deposition.

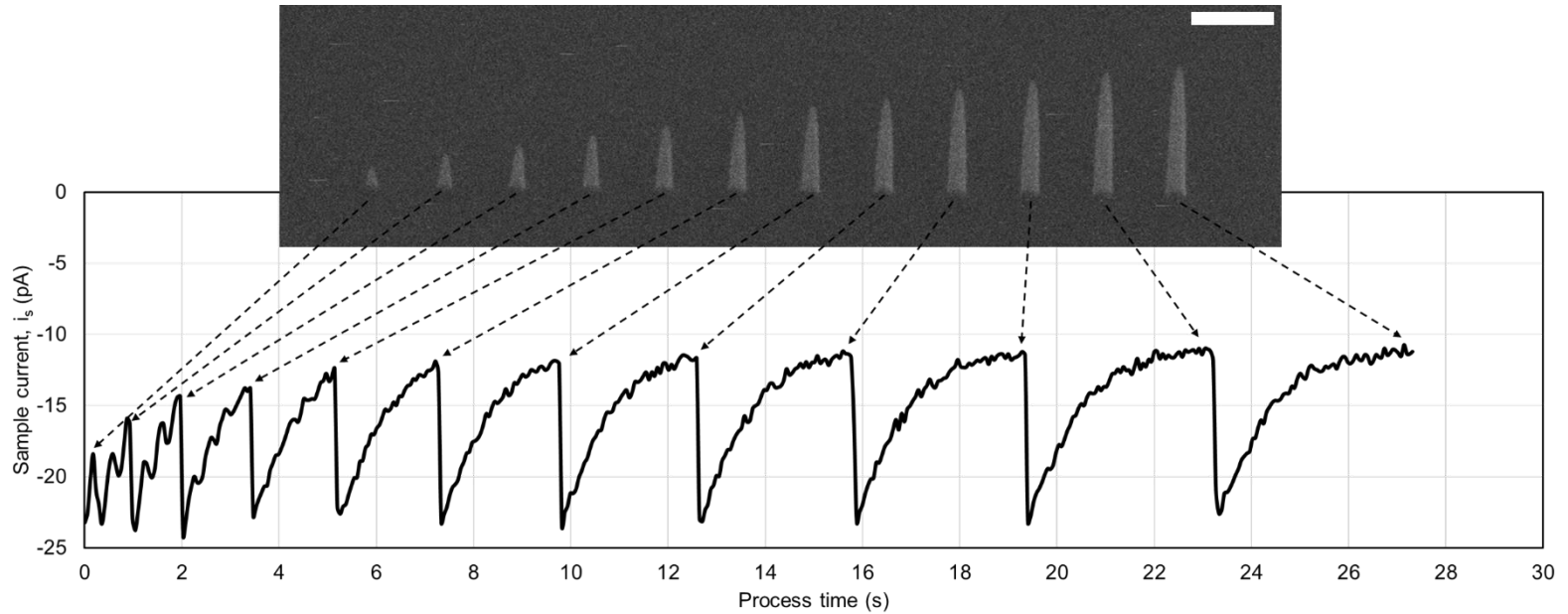


Figure 4-1 Pillar evolution during FEBID and the accompanying sample current trace collected via the sample stage. Dash arrows point to each pillar's current trace. A conical tip on a conical shaped is observed as the pillar height increases. The pillars are deposited by a 30 keV 32 pA beam. The design and (measured) pillar heights from left to right are: 50 (86), 100 (159), 150 (204), 200 (245), 250 (286), 300 (340), 350 (390), 400 (449), 450 (489), 500 (521), 550 (562), 600 (598) nm. The secondary electron image was acquired at a substrate tilt angle of  $52^\circ$  to see the cross-sectional profile of the nanostructure. Scale bar = 200 nm.

#### 4.1.1 Pillar

Pillar deposition ensues when the focused electron beam is held stationary on the substrate surface under the steady flow of organometallic precursor to sustain deposition. Initially, the pillar takes on the shape of the Gaussian shaped electron beam while later, when the diameter of the pillar becomes constant, it is determined by the convolution of the electron interaction volume with the deposit volume. Thus, during the early stages of pillar growth a conical shaped feature first forms on the substrate. As growth ensues and the pillar elongates, a cylindrical shaped feature (broadening) of the pillar forms underneath the cone as shown in Figure 4-1. The cylindrical base of the pillar has a nominal diameter of approximately 20 - 100 nm depending on the primary electron beam energy and the beam current. It is observed under most circumstances that the pillar vertical growth rate decreases with increasing pillar height. The vertical growth rate of each of the pillars from left to right is: 495, 275, 221, 177, 173, 171, 161, 162, 160, 150, 150 and 150 nm/s. Deposition rate is highest during the initial cone tip growth and steadily decreases with deposition time. The sample current collected through the electrically conducting stage during pillar deposition (Fig 4-1) captures the deposition rate deceleration as a decrease in the positive slope of the sample current versus time curve. Similar observations have been previously made [75].

#### 4.1.2 Transition

Soon after the prescribed pillar height is reached, as specified by computer-aided design (CAD) design discussed later, the deposition of the segment element of the calibration structure begins. Segment deposition begins at the instant that the electron beam begins lateral scanning. The segment growth initiates at the tip of the pillar which coincides with the pillar nanowire center axis. The transition length is roughly equal to the radius of the pillar, especially for relatively higher primary electron beam energies where the elastic scattering probability is low. Importantly, the angle at which the segment grows is determined by the digital beam scan speed. In order to establish a constant beam speed, and therefore define a linear nanowire, the pixel point pitch ( $\Lambda$ ) is kept fixed at 1 nm while the pixel dwell time ( $\tau_d$ ) is adjusted to obtain the necessary beam speed. The sequence of exposure positions and dwell times required to deposit a calibration structure is assembled as a table, a so-called stream file, and written in text format for upload to the dual beam microscope to execute deposition.

#### 4.1.3 Segment

A straight and linear segment is the expected outcome when a constant beam speed is specified in the exposure file. The linear segment design is defined by the segment angle ( $\zeta$ , see Figure 4-2a) which is the angle spanning the segment growth vector, projected into the substrate plane, and the true 3D segment growth vector. However, it is observed in experiments that ( $\zeta$ ) steadily decreases as deposition progresses (Figure 4-2b inset).

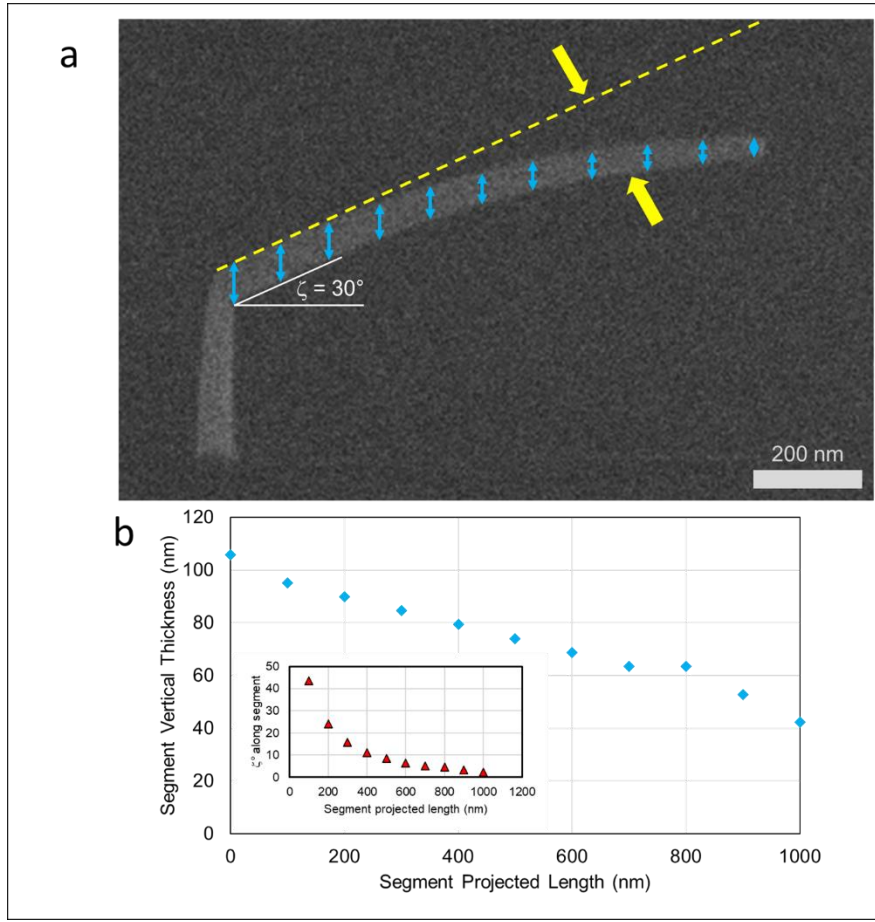


Figure 4-2 (a) An electron micrograph of a calibration structure with a segment angle of  $\zeta = 30^\circ$ , acquired at an angle of  $52^\circ$  with respect to the substrate surface normal. The pillar = 400 nm and total projected segment length,  $b_{x,y} = 1000$  nm. The segment element is aligned with the tilt axis in the image. The discrepancy between the design and deposit is realized as a downward deflection of the segment with respect to the linear design shown by the superimposed yellow dash line and arrows. The blue double arrows indicate the decrease of vertical segment thickness with increase in segment length. (b) A plot of the vertical segment thickness,  $b_z$  variation with elongation. Inset: Changing  $\zeta$  along the projected segment length;  $\zeta = \text{atan}(b_z/b_{x,y})$ .

This observation is correlated with a decrease in the vertical thickness, ( $b_z$ ) along the segment shown by the blue arrows in Figure 4-2a. These characteristics combine to produce a segment that deflects toward the substrate instead of the intended path as shown by the yellow dash line and arrows in Figure 4-2a. The maximum segment thickness ( $b_z = 105$  nm) is measured adjacent to the pillar and steadily decreases along the segment length with the minimum ( $b_z = 42$  nm) observed at the final beam impact region, or BIR. As a result, ( $\zeta$ ) is not sustained along the segment (Figure 4-2b inset). This variation in angle and thickness compounds in more complex structures, e.g., a multi-level structure consisting of a network of interconnected segments, and often leads to failure or significant distortion ultimately rendering the final deposit useless.

## 4.2 Calibration Structure Array

Access to a wide range of 3D mesh style objects is one of the advantages of nanoprinting using FEBID. The 3D mesh objects are attained by control of two electron beam modes: the spot, or stationary, mode and the scanning mode. Results in section 4.1 show the calibration style elements deposited by the two electron beam modes (pillar and segment). In comparison, nanowires with varying complexity are achieved by scanning the electron beam, while the spot mode is limited to nanowires which are vertical and coaxial with respect to the beam.

Control of the scanning electron beam by varying the pixel dwell exposure time ( $\tau_d$ ), at constant pixel point pitch ( $\Lambda$ ), results in segment elements deposited at different angles ( $\zeta$ ) as shown in Figure 4-3a. These segments have a common total length (400 nm)

but exhibit a prescribed angle variation ranging from  $\zeta = 12.5^\circ$  to  $80^\circ$ . As the digital beam speed decreases the segment angle increases. For example, in Figure 4-3a, the  $12.5^\circ$  segment was deposited at a scanning speed of 1200 nm/s and 70 nm/s for the  $80^\circ$ .

Other than increasing the angle, longer dwell times result in higher volume deposition rates per exposure pixel. Thus, the segment thickness and width increase with the angle. This variation in deposit thickness illuminates some electron scattering-deposit convolution characteristics. For instance, the segment tip, marked by a yellow dash circle in Figure 4-3a, develops a sharper edge as the angle, and hence the deposit volume increases. In other words, as the segment angle increases the calibration structure is tending toward the pillar geometry as  $\zeta \rightarrow 90^\circ$ . It should also be point out that the total deposit volume occurring underneath the segment element of the deposit, on the substrate, decreases as the segment angle increases. This occurs because the increase in segment thickness causes additional elastic scattering that broadens the electron probe that ultimately strikes the substrate surface. Electron probe current density, i.e., the number of electrons per unit area per unit time, decreases thereby decreasing the deposition rate on the underlying substrate. As indicated in section 4.1, the segment thickness tapers with segment elongation. Figure 4-3b shows the tapered effect for  $12.5^\circ$ ,  $25^\circ$ , and  $50^\circ$  segments. Further characterization of the thickness variation is shown in section 4.5.

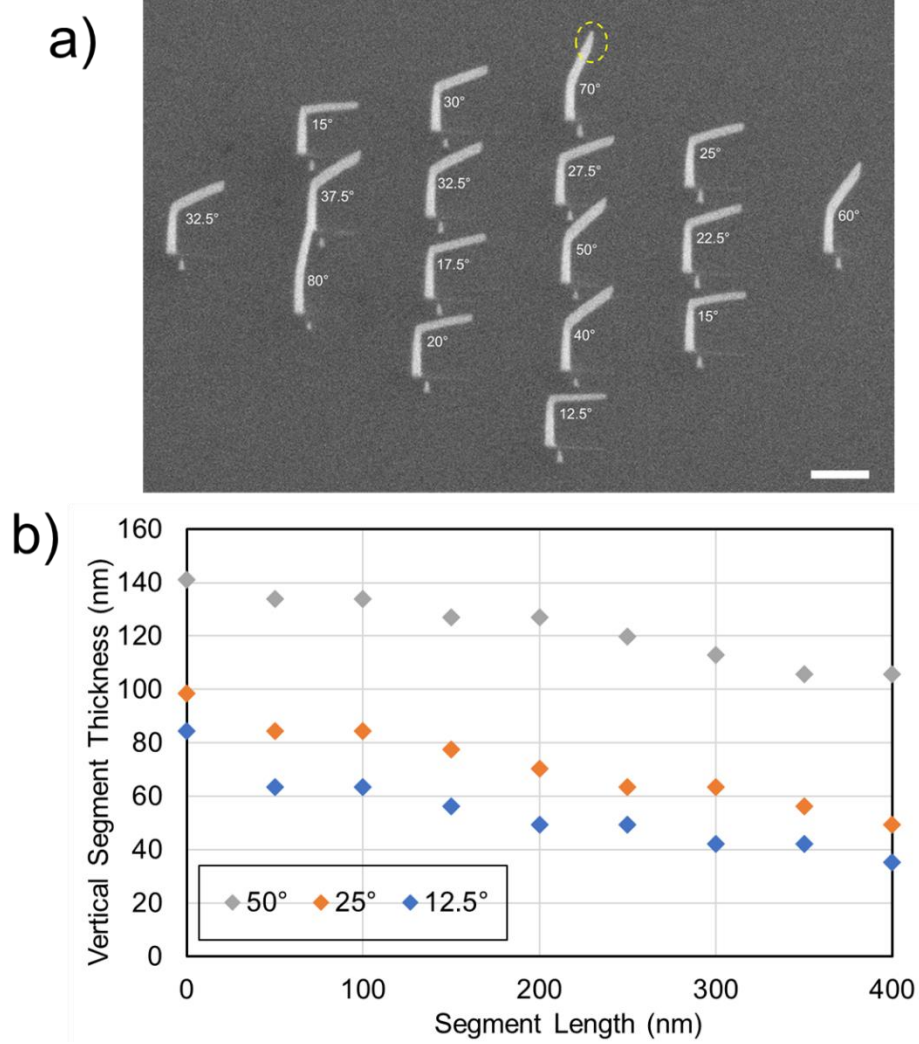


Figure 4-3 (a) SEM image of a calibration structure array at 52° tilt view. Pillar = 400 nm, segment = 400 nm, and segment angles ( $\zeta$ ) ranging from 12.5° to 80°, and  $\zeta$  is indicated on the image. The order of deposition is randomized. The yellow circle marks the last beam impact region (BIR) where the segment terminates. (b) Vertical segment thickness measured at 0 nm to 400 nm projected segment length with 50 nm increments for  $\zeta = 12.5^\circ$ ,  $25^\circ$  and  $50^\circ$ . Scale bar = 400 nm.

### 4.3 Calibration Structures at 30 keV and 7.5 keV

The elastic scattering electron interaction volume plays a key role in determining both the vertical growth rate and volumetric deposition rate during 3D nanoprinting. The scattering volume is a strong function of primary electron beam energy and decreases with decreasing energy. Thus, experiments were conducted at two different primary electron beam energies. In one case, at 30 keV, the penetration depth of the electron interaction volume is much larger than the calibration structure height. Importantly, the reference frame for penetration depth is taken as the penetration depth in a bulk sample of PtC<sub>5</sub>, where  $R_E = 5820$  nm (Figure 2-7). In contrast, the penetration depth,  $R_E = 580$  nm, is on the order of the deposit height at 7.5 keV. To best study the effects of change in the electron interaction volume alone, calibration structures are deposited using a 30 keV and 7.5 keV beam energies at comparable beam currents, 32 pA and 37 pA, respectively. The summary of the results derived from these experiments are now reported.

In Figure 4-4 the vertical growth rate (VGR = 190 nm/s) measured at 7.5 keV is higher compared to the growth rate of 130 nm/s measured at 30 keV. For this reason, the resulting pillars are longer at 7.5 keV. The relatively larger penetration depth for the 30 keV electron beam deposits results in pillars with sharper and longer conical shaped tips. In contrast, at 7.5 keV, the pillar apex appears smaller and rounded (green arrows in Figure 4-4). The segments at 30 keV are thicker in the vertical coordinate compared to segments deposited at 7.5 keV. For instance, for the  $\zeta = 50^\circ$  segment, the vertical thickness at 30 keV is 134 nm while at 7.5 keV it is 98 nm. Also, at the final tip of the

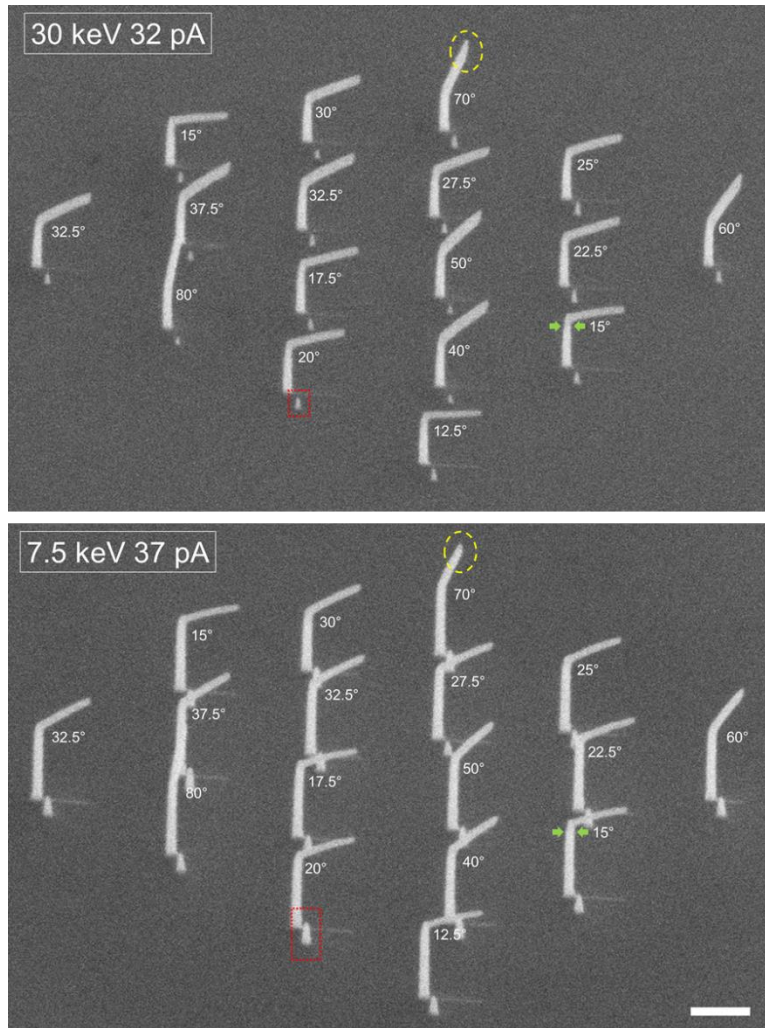


Figure 4-4 Arrays of calibration structures deposited at 30 keV 32 pA and 7.5 keV 37 pA highlighting effects of energy-dependent electron interaction volume, such as deposit shape, (indicated by arrows for the pillars and yellow dash circles on the segment) and deposit growth rate (marked in red). Both SEM images were captured at the same field of view at 52° stage tilt. Prescribed design parameters for pillar height and segment length = 400 nm. Scale bar = 400 nm.

segment (yellow dash circle in Figure 4-4), the edge is more rounded at 7.5 keV while at 30 keV it is a sharp edge. The shape of the segment tip for both cases is consistent with the convolution expected between the electron scattering volume. For example, the lower probability of electron scattering at 30 keV is manifested as a sharp cone at the beam impact region as the deposit volume mimics the narrow scattering profile which effectively imprints into the growing deposit. For the same reason, a broad tip emerges at lower energy as the incident deviates more quickly off the initial beam trajectory limiting penetration and rounding the apex.

Lastly, the initial deposition rate was evaluated for both voltages using a brief exposure time, separated from the calibration structure element, as a reference deposit (marked red in Figure 4-4). The purpose of the reference is to determine the maximum deposit rate which occurs at beginning of exposure. As expected, the vertical growth rate at 7.5 keV was found to be  $1.83 \times 10^9$  nm/s and is higher than the value measured at 30 keV of  $9.8 \times 10^8$  nm/s. The reference exposure was conducted using a single pixel exposure time of 0.0002 ms for all voltages indicates that the 7.5 keV beam has a higher growth rate.

#### **4.4 Sample Current Characterization**

In general, EBID experiments are mainly characterized by scanning electron imaging from which representative geometric factors are extracted. However, this characterization is carried out post-deposition and limits the ability to reconstruct the reaction–transport dynamics taking place during deposition. Thus, any information that can be gathered dynamically during the growth process would provide an informative data

stream to enhance an understanding of the FEBID process. Such results can be compared with 3D simulations of EBID to test simulation accuracy and robustness. Importantly such a data stream could perhaps be used to dynamically correct deposition *in situ*.

Conveniently, the net number of electron species absorbed during the deposition process provide real-time information about the growing nanostructure. This quantity can be captured by monitoring the dynamic sample current through the sample stage. This data stream is referred to here as sample current,  $i_s$ . An example is presented in Figure 4-5 demonstrating a sample current measurement and the sensitivity of such a measurement to unexpected changes in mesh object geometry.

Figure 4-5a shows the intended deposit geometry based on CAD along with an image of the final deposit. A poor replication of the CAD resulted. The resulting sample current trace collected during the experiment is shown as the red data trace in Figure 4-5c. The sample current trace evolution was found to be sensitive to deposit quality when compared with the sample current trace that resulted from a successful deposition.

The final mesh object model deposit differs in the two experiments shown due to a different time order of exposure for each nanowire constituting the model. Exposure order is indicated in the CAD by color according to level of exposure. The exposure level order follows the color sequence blue (level 1), light blue (level 2), yellow (level 3) and red (level 4). The color order then repeats for levels 5 – 8, and so on. In design Figure 4-5a, the segment order for exposure was erroneously assigned. Importantly, the exposure instructions for beam displacement include only movements in the substrate plane. Thus,

exposure must be laid out in design such that deposit–beam intersection is always preserved. This was not the case for the design displayed in Figure 4-5a. Specifically, the exposure error occurred on exposure level 2(light blue), where multiple segment depositions were requested without a supporting, underlying feature – the deposit collapsed. This error is captured by SEM imaging but also on the sample current trace (red). On the other hand, Figure 4-5b presents an optimized CAD layout where each segment requested for deposition has a supporting nanowire that was exposed on a previous exposure level. Lastly, it is important to note that when multiple segments are specified for deposition on a single exposure level, e.g., on the level 2, Figure 4-5b, these segments are exposed in parallel as opposed to being grown one at a time; one pixel is exposed per segment before advancing the primary electron beam forward for the next pixel.

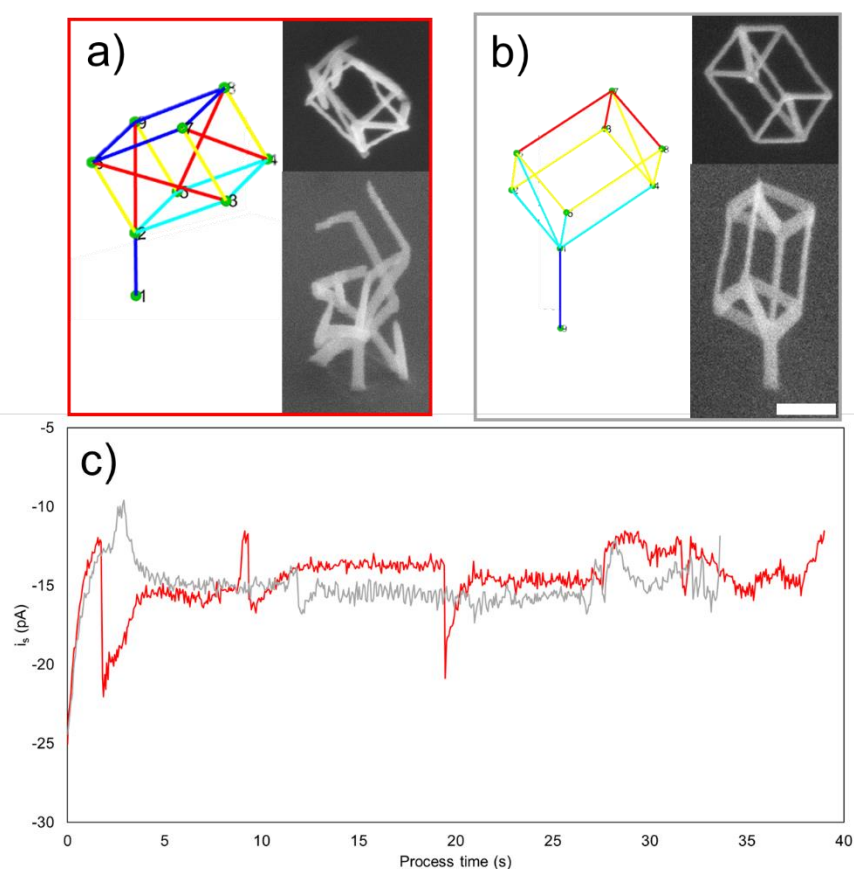


Figure 4-5 3D FEBID illustration of a rectangular prism CAD design model, the subsequent experimental deposit and *in situ* stage sample current collected during deposition using 30keV 32 pA beam. In (a) and (b) the colors on the CAD design represent exposure levels; blue (level 1), light blue (level 2), yellow (level 3), and red (level 4). The SEM images show the final deposits. The top images are captured from a top-down view and images at the bottom from 52° stage tilt. The prism is oriented at 45° on the supporting pillar. Length = 400 nm, width = 200 nm, height = 200 nm, and a diagonal across the short face of the prism. (a) Demonstrates poor CAD design replication due to incorrect exposure level assignment, and (b) shows accurate design replication. (c) Traces of sample current collected during deposition of (a) – red and (b) – grey. Scale bar = 200 nm.

#### **4.5 Sample Current Data for a Single Calibration Structure**

Experiments revealed that calibration structures deposited with a variable segment angle exhibit a unique sample current signature trace. The deposit rate is known to change as a function of segment angle according to SEM imaging therefore the fact that the sample current trace also changes suggests a correlation between these phenomenon. Further, the change in the collected number of electrons seems to correlate with deposition rate changes. A closer inspection of a single sample current trace reveals that the pillar and segment exposure elements can be identified and separated.

The sample current trace presented in Figure 4-6c captures the three distinct growth stages of a calibration structure: pillar, transition, and segment as defined by the author. The stages are delineated in time and are color coded in the figure.

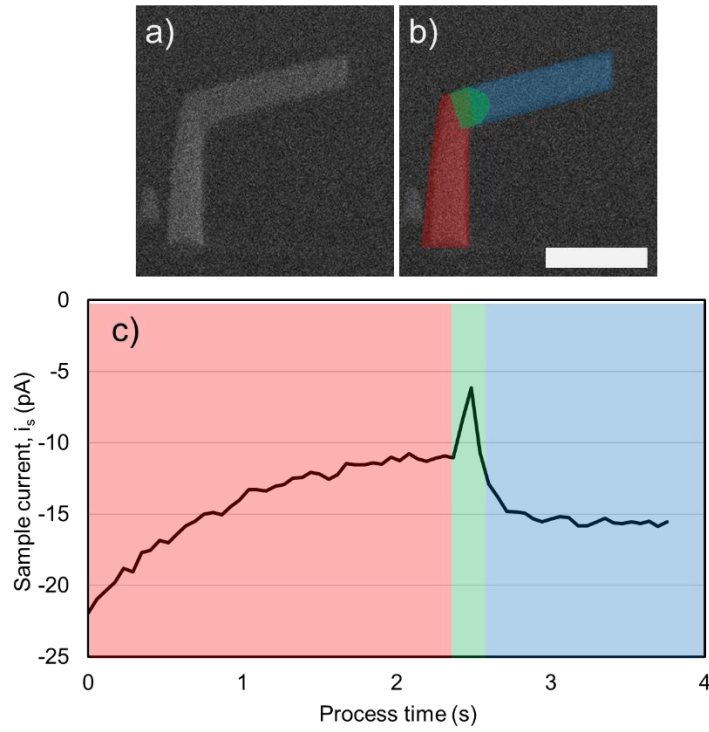


Figure 4-6 A pillar and segment calibration structure. The stages of deposition are ‘pillar’, ‘transition’ and ‘segment’. Pillar deposition occurs using stationary electron beam exposure. The electron beam moves at constant, digital beam velocity during ‘transition’ and ‘segment’ growth. The pillar and segment are both 400 nm in length. (a) An electron micrograph of a calibration structure (scale bar = 300 nm) acquired at an angle of  $52^\circ$  with respect to the substrate surface normal. (b) False color image of (a) to point out the three distinct growth stages also captured in (c). Experiments were conducted using a beam acceleration voltage of ( $E_0$ ) 30 keV and a beam current of ( $i_b$ ) 32 pA. (c) The sample current ( $i_s$ ) collected through the substrate during FEBID is sensitive to geometric changes during growth. The continuous black sample current profile was collected during deposition of (a) that yielded a segment angle of  $\zeta = 30^\circ$ .

#### 4.6 Sample Current Traces for an Array of Calibration Structures

Figure 4-7 shows sample current ( $i_s$ ) traces, or profiles, collected during the experimental deposition of calibration structures with a variable segment angle spanning  $12.5^\circ$  to  $80^\circ$ . Experimental variation in calibration structure deposition is qualitatively represented in Figure 4-7 by including stage current traces from multiple experiments for the case of ( $\zeta = 15^\circ$ ) and ( $\zeta = 32.5^\circ$ ).

The following analysis places emphasis on the relative differences observed in the sample current traces when the segment angle ( $\zeta$ ) is varied. Clear comparisons between sample current traces are difficult to discern with many overlapping traces. Thus, to make relative comparisons between experiments each current profile has been shifted vertically by a current displacement of  $\Delta i_s = 2 \text{ pA}$  in Figure 4-7. As an example of the magnitude of the sample current expected, the sample current trace representing ( $\zeta = 12.5^\circ$ ) has not been shifted and thereby representing an example of a raw stage current data profile expected for the primary electron beam condition 30 keV and 32 pA, typical for 3D FEBID.

The total processing time required to deposit a calibration structure of a constant length ( $S = 800 \text{ nm}$ ) differs depending on the segment angle. For example, segments with relatively larger ( $\zeta$ ) require a longer total processing time to deposit the segment feature – as the digital beam speed ( $v_b$ ) is reduced, fewer pixels are exposed for a longer total beam dwell time favoring vertical growth over lateral displacement. The electron dose per unit scan length ( $i_b \tau_d / q \Lambda$ ) increases leading to more deposition per pixel ( $q = 1.6 \times 10^{-19} \text{ C/e}^-$ ).

As the segment angle increases, the total volume deposited per displacement (pixel point pitch,  $\Lambda$ ) increases with a complementary increase in the surface area per unit length. Consequently, more experiments revealed that more SEs are emitted driving the current signal more positive in the ‘segment’ stage of growth as ( $\zeta$ ) increases. Lastly, the segment width is observed to increase with ( $\zeta$ ) (Figure 4-9).

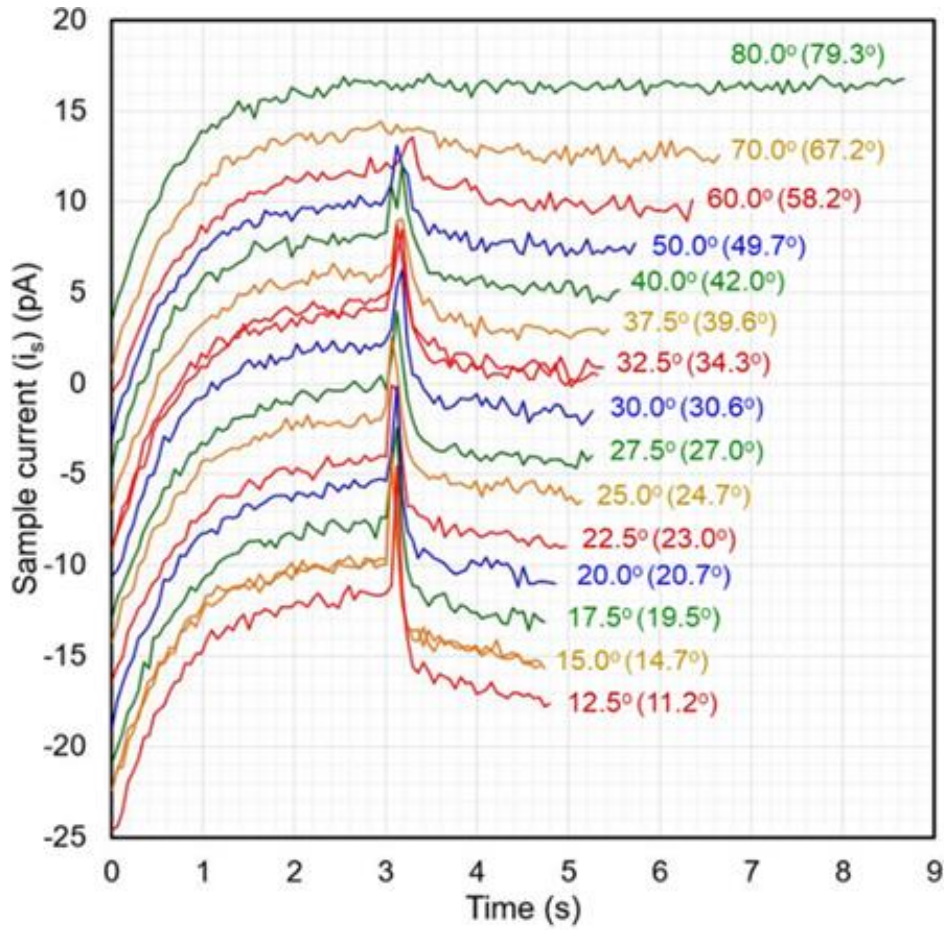


Figure 4-7 Segment angle changes are resolved in time–dependent sample current profiles collected during FEBID. In each experiment, a 400 nm pillar was deposited followed by the deposition of a segment 400 nm long; the so–called ‘calibration structure’ using  $E_0 = 30$  keV and  $i_b = 32$  pA. Only the segment angle ( $\zeta$ ) was varied among the experiments. Each angle dependent profile has been shifted along the y–axis to create a separation of  $\Delta i_s = 2$  pA between each profile to avoid profile overlap and clarify trends. The sample current profile collected for the case of  $\zeta = 12.5^\circ$  was not shifted and provides a true sample current profile. The 3BiD [38] specified segment angle is shown for each curve followed by the measured value of ( $\zeta$ ) after deposition.

#### 4.7 Sample Current Traces for Calibration Structures at 30 keV and 7.5 keV

Calibration structure experiments were also conducted using a 7.5 keV primary electron beam energy. Importantly, as stated previously, these experiments were contrived to isolate for electron interaction volume effects by selecting similar primary electron beam currents for deposition, namely 37 pA for 7.5 keV and 32 pA for 30 keV. Using this approach, the study reduces to one that compares the effect of beam energy. Further, to control for the effect of beam energy more clearly, the growth parameters were kept constant for both experiments. For example, the pixel point pitch was 1 nm and a similar segment angle range was attempted 12.5° to 80°. The calibration structure total length was ( $S = 800$  nm) with a 400 nm length pillar and a 400 nm segment span. Finally, similar to the 30 keV case, sample current was collected for all segment angles.

The three distinct stages of calibration structure deposition, namely the pillar, transition, and segment stages, were also resolved in the ( $i_s$ ) vs ( $t$ ) data at 7.5 keV (Figure 4-8). However, there are also marked differences in the growth characteristics produced at the two primary electron beam energies concurrent with the characteristics of their respective beam energies. In the pillar deposition stage at 7.5 keV, the sample current has a steep rise during the initial stages of growth followed by a more distinct plateau compared to that observed at 30 keV. Please note, in the following analysis of results an ‘increase’ in sample current will refer to a positive change in current. This trend is also observed when the beam is incident on the planar Si substrate, where the primary electron current is reduced from -37 pA to -20 pA, a 46 % decrease compared to a 22% decrease at 30 keV.

Sharp sample current spikes, or peaks, are also observed in the 7.5 keV current traces at the transition stage of growth, from pillar to segment, but the magnitude of the peak is smaller when compared to the transition peaks observed in the 30 keV data. Beyond transition deposition, the abrupt decrease in sample current at the beginning of the segment growth stage is more drastic at 7.5 keV. Further, the sample current exhibits a steady decrease as segment growth progresses; more prominent than the decrease seen at 30 keV.

In keeping with experimental trends reported for the 30 keV data, the individual current traces in the 7.5 keV graph have been shifted by 2 pA relative to each other, but 12.5° data trace has not been shifted and represents the actual, raw sample current data. Two data traces are presented for segment angles of 15° and 32.5° to demonstrate experimental variation.

In general, it took a relatively shorter total processing time to deposit the calibration structures, per unit length, at 7.5 keV relative to 30 keV. For instance, it took 7.6 s to deposit the 80° segment at 7.5 keV versus 8.6 s to deposit the complementary 30 keV structure.

These results show that the case presented using the 30 keV beam can be used to generalize 3D FEBID process. Using 30 keV as the reference electron beam energy, combined with the understanding of various beam energies and their interactions solidifies the conclusions reported here using the 30 keV beam.

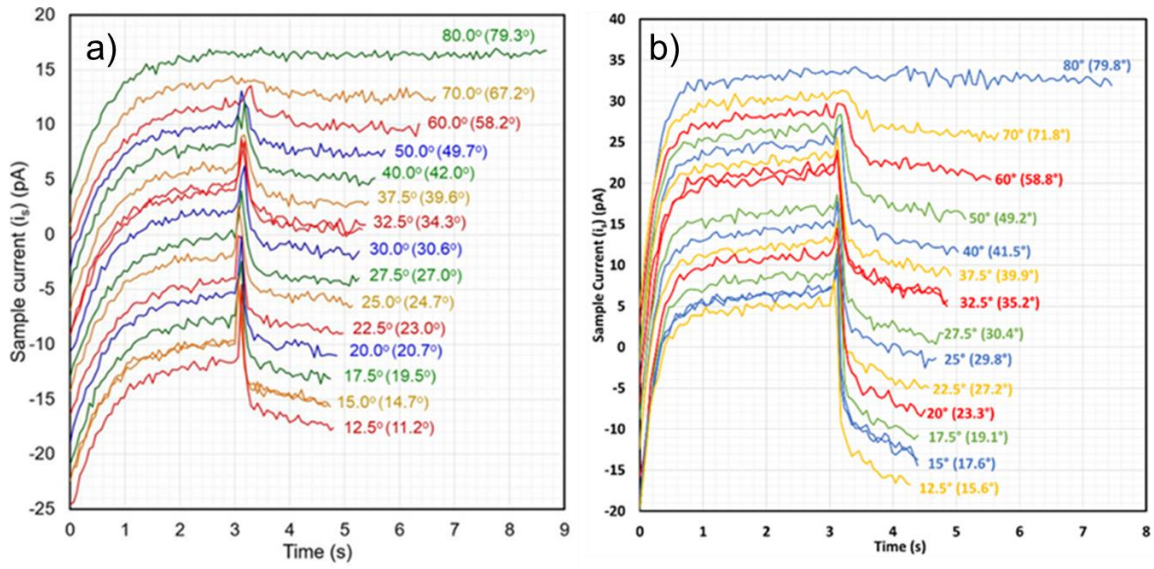


Figure 4-8 A comparison of sample current traces collected during calibration structure array deposition shown in Figure 4-4. Each calibration structure total length was ( $S = 800$  nm) with a 400 nm length pillar and a 400 nm segment.

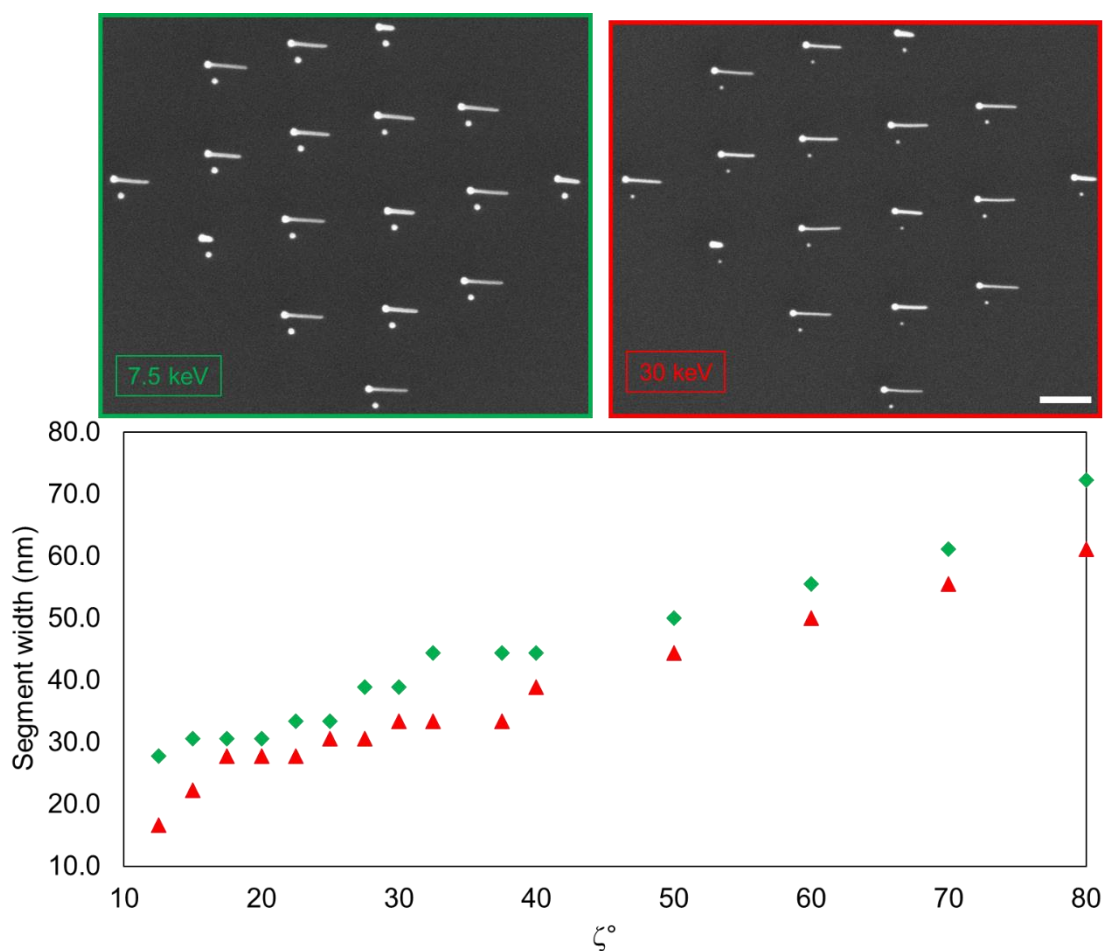


Figure 4-9 Electron interaction volume effects in 3D FEBID. Segment width is measured across the segment from a top-down view on the SEM images. Segment width increases with increasing ( $\zeta$ ), and more generally, with decreasing electron beam energy. The electron micrographs are the top-down view images of Figure 4-4. Scale bar = 400 nm.

#### 4.8 3D FEBID Calibration Structure and Sample Current Simulations

3D FEBID simulations, which include electron trajectories, precursor consumption and replenishment, and electron dissociation cross sections, reproduce experiments to facilitate better understanding of FEBID growth characteristics.

The 30 keV and 7.5 keV experiments are reproduced using simulations to further elucidate electron interaction volume effects on FEBID deposits and the consequent influence on the sample current as shown in Figure 4-9. A total calibration structure length of ( $S = 1200$  nm) with 400 nm pillar and 800 nm segment is simulated for  $\zeta = 30^\circ$  and  $60^\circ$ . The virtual SEM images of the calibration structures are acquired at  $52^\circ$  with respect to the substrate surface normal, and the segment cross-section images (inset) are taken normal to the calibration structure axis. Akin to observations from experiments, segment cross-section images show volume deposition rate increase with increasing segment angle resulting from longer dwell times at higher angles. Segment tapering, deflection, and failure ( $\zeta = 30^\circ$  at 7.5 keV) is also observed in the simulation results.

The simulated sample current reveals all the calibration structure features identified in the experiments, that is, pillar, transition, and segment. Simulations also provide the coefficient of SE emission data which is not accessible by experiments. SE emission coefficient (SE yield) is given as  $\delta = i_\delta/i_b$ , where  $i_\delta$  is the total SE emission current and  $i_b$  is the PE current of incident electron beam. The SE yield captures the evolution of the calibration structure elements during deposition and defines the simulated sample current.

The less energetic 7.5 keV primary electron beam has a higher SE yield than the 30 keV beam because it experiences more near surface scattering events.

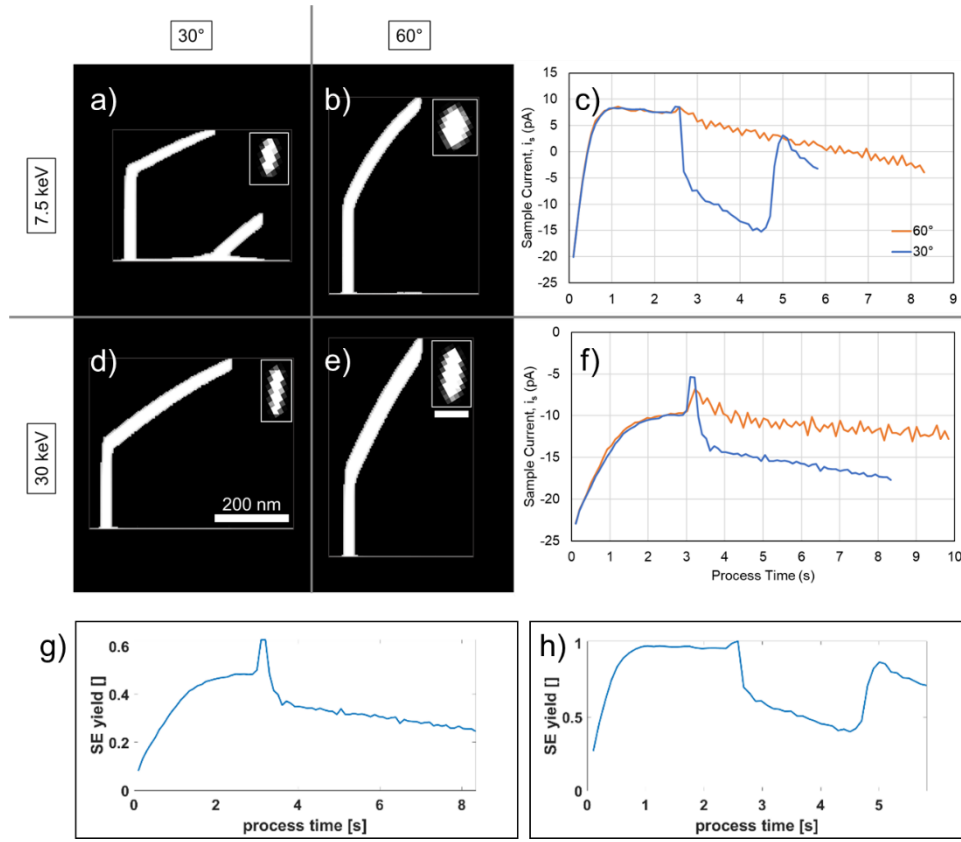


Figure 4-10 3D FEBID calibration structure and sample current simulations using 30 keV 32 pA and 7.5 keV 37 pA primary electrons. The simulations are generated using the 3BiD CAD [38] environment and the supplementary Simulation package [37]. The virtual calibration structures are designed such that the pillar = 400 nm and segment = 800 nm at  $\zeta = 30^\circ$  and  $\zeta = 60^\circ$ . (a)  $\zeta = 30^\circ$  at 7.5 keV, (b)  $\zeta = 60^\circ$  at 7.5 keV, (d)  $\zeta = 30^\circ$  at 30 keV and (e)  $\zeta = 60^\circ$  at 30 keV are virtual SEM images of the calibration structure cross-section sliced along the total structure length (S), and (Inset) normal to the segment element. The cross-sections reveal the beam-deposit interaction volume. (c)  $E_0 = 7.5$  keV, and (f)  $E_0 = 30$  keV are the sample current traces dictated by the secondary electron (SE) yield. The SE yield traces along the deposit during growth at (g) 30 keV and (h) 7.5 keV for  $\zeta = 30^\circ$  are shown. Inset scale bar = 50 nm.

## Chapter 5: Discussion

### 5.1 Effects of Electron Beam Interaction Volume

Electron elastic and inelastic scattering determines the shape and size of the electron-deposit interaction volume. While elastic scattering is described by negligible energy loss, the characteristic high scatter angles result in electron straggle which influences the shape and size of the interaction volume. Conversely, inelastic scattering exhibits small scatter angles and causes energy transfer to the solid. The shape and size of the interaction volume alter the secondary and backscattered electron emission profiles. With this perspective, the electron energy dependent shape of the calibration structure is explained.

The Kanaya-Okayama electron range,  $R_E$  (Equation 2-4) in bulk PtC<sub>5</sub> for a 7.5 keV beam is 580 nm and for 30 keV is 5820 nm (Figure 2-7). Considering the vertical thickness of the calibration structure, 400 nm pillar and an average of 100 nm for the segment, the effects of the near surface electron scattering of the 7.5 keV electron beam versus the narrowly scattered 30 keV are discussed for experiments and simulations results.

The near surface interaction volume of the 7.5 keV beam results in a large areal secondary electron flux compared to the 30 keV primary electron beam. Consequently, the precursor dissociation rate increases leading to a high volume and vertical growth rates for the lower energy. For instance, the growth rate at the initial stages of pillar formation on the bulk SiO<sub>2</sub>/Si substrate at 7.5 keV ( $1.83 \times 10^9$  nm/s) is two times higher than at 30 keV

$(9.8 \times 10^8 \text{ nm/s})$ . SE emission from the bulk substrate and equilibrium precursor surface coverage contribute to the high pillar formation rate, and the interaction volume of the two energies results in the varying rates. The final vertical growth rates are 190 nm/s and 130 nm/s for 7.5 keV and 30 keV, respectively.

The shape of the pillar and segment tip for both electron energies is consistent with the convolution expected between the electron scattering volume. The minimally scattered 30 keV electron is revealed as a sharp cone at the beam impact region on the pillar and the segment deposit volume mimics the narrow scattering profile. Similarly, a rounded tip emerges at lower energy as the incident electron diverges more quickly off the initial beam trajectory limiting penetration and rounding the apex. (inset in Figure 4-10). The 30 keV electron trajectories that are barely scattered transmit through the segment and create more scattering events at the exit edge. Fowlkes et al.[17] found that these SEs liberated by the transmitted beam contribute the most toward segment growth and hence the segment thickness. As a result, the elliptical-like cross-section of segments deposited at higher energy tend to have axis such that the length of the major axis,  $2a$  is much greater than the length of the minor axis,  $2b$ . For a  $30^\circ$  segment deposited by a 30 keV beam,  $2a = 95 \text{ nm}$  and  $2b = 30 \text{ nm}$  compared to  $2a = 70 \text{ nm}$  and  $2b = 40 \text{ nm}$  at 7.5 keV where  $a$  and  $b$  are measured at 100 nm projected segment length.

## 5.2 Sample Current Equations

The sample current collected during electron irradiation of a flat substrate surface is described by;

$$i_s = i_b - \delta_I i_b - \eta i_b - \delta_{II} \eta i_b \quad (5-1)$$

and serves as the reference configuration for understanding the current collected for a 3D object. ( $i_b$ ) is the primary electron beam current, ( $\delta_I$ ) is the fraction of the beam current lost as emitted SEs during primary beam impact, ( $\eta$ ) is the electron fraction lost as backscattered electrons, and ( $\delta_{II}$ ) secondary electrons emitted due to backscattered electron emission.

In the context of 3D FEBID, Equation 5-1 requires minor revision to;

$$i_s = i_b - \delta_{IA} i_b - \eta i_b - i_b (\delta_{IB} \eta_f + \delta_{II} \eta) \quad (5-2)$$

In this case, a fraction of the primary electron population is emitted from the 3D deposit toward the substrate and may excite SEs during emission. These are the forward scattered electrons ( $\eta_f$ ). As a further classification,  $SE^A$  electrons are emitted during the initial primary beam impact while  $SE^B$  electrons are emitted by forward scattered electrons and are defined only for the case of complex 3D surfaces [17].  $SE^B$  electrons are a direct consequence of the deposit–electron scattering volume convolution and contributes significantly to defining the characteristic shape of the stage current curve. Finally, the fraction of  $SE^A$ s lost is  $\delta_{IA} = SE^A_s / \delta_I$  and the fraction of  $SE^B$ s lost is  $\delta_{IB} = SE^B_s / \delta_I$ .

### 5.3 7.5 keV and 30 keV Sample Current

As mentioned in the method chapter, comparable electron beam currents were selected for both electron beam energies: 32pA for 30keV and 37pA for 7.5keV. The sample current detected on the substrate for the two energies were:  $i_s(30\text{keV}) = 25\text{pA}$  and  $i_s(7.5\text{keV}) = 20\text{pA}$ . In general, the confinement of the interaction volume to the near surface region at the primary electron beam energy of 7.5 keV leads to the ejection of a larger number of both SEs and BSEs, relative to the emitted number at 30keV. The higher SE and BSE yields act to decrease ( $i_s$ ) according to Equation 5-1 as shown in Figures 4-9g and 4-9h.

The initial increase of the vertical growth rate captured by the slope of the sample current,  $di_s/dt$ , is caused by the translation of the electron interaction volume from the bulk substrate to emerging  $\text{PtC}_5$  pillar. The derivative  $di_s/dt$  is relatively larger at 7.5keV, between 0 - 1 s of deposition, since the areal density of electron species emitted is larger than at 30 keV – the time averaged density of electron species in the pillar, per unit height, is larger at 7.5 keV. This is shown on the plot (Figure 4-8b) as a decrease in the negative value of the sample current, which increases to a positive value ( $i_s > 0$ ). An abundance of SEs are liberated at the surface at 7.5 keV efficiently dissociating the surface adsorbed precursor molecules. Unfortunately, the elevated dissociation rate also induces a large precursor surface concentration gradient, directed vertically along the pillar. Nonetheless, a higher growth rate is observed for the lower electron beam energy.

Eventually, as the pillar deposition ensues, the entire interaction volume is contained within the pillar, with few primary electron species transmitted from pillar to substrate via the solid phase only. At this point, if precursor is plentiful on the surface and unchanging with height, the vertical growth rate should reach a steady-state value. Although the sample current does steadily increase as a result of higher magnitude of the emitted SEs (Figure 4-8) the rate of sample current change is sub-linear. This indicates that the vertical growth rate is continuously decreasing (a decrease in  $di_s/dt$ ), and not constant. This steady decline in the vertical deposition rate suggests precursor-limited conditions. Precursor-limited conditions develop when the precursor surface coverage in the beam interaction volume is less than the maximum value.

Direct replenishment from the gas phase to the beam impact region is inadequate to replenish the precursor completely. Conveniently, the development of a precursor surface gradient, due to continuous dissociation, leads to an additional precursor source via precursor surface diffusion. Transport occurs down the concentration gradient. Unfortunately, this source can be compromised as, the surface-bound precursor molecules that would have contributed to vertical growth, are consumed by the SEs generated along the pillar surface, below the beam impact region, effectively broadening the pillar. The current data suggests that these limitations diminish the effectiveness of this precursor supply, explaining the exponential decay of  $di_s/dt$ .

To a certain extent, the increase in the sample current is merely a result of an increase in SE emission, but the vertical growth rate is directly related to the convolution

of the deposit and the electron interaction volume. Eventually,  $di_s/dt$  saturates and tends to a plateau (Figure 4-8) depending on the pillar height [68, 74, 76], which determines when the electron interaction volume contained within the pillar approaches quasi-steady-state [77].

#### **5.4 Electron Capture via Ga<sup>+</sup> Milled Substrate**

To minimize the influence of electron scattering by the underlying substrate, and to focus in on electron scattering only by the growing segment, electron capture experiments were designed to mimic, to an extent, a Faraday Cup. Ion milled trenches would reduce the probability of scattered electrons escaping from the substrate. This would create a pathway to understating the intrinsic mechanisms that cause the continuous sample current decay,  $di_s/dt < 0$ , during segment growth.

30° segments were deposited over ion milled trenches on the SiO<sub>2</sub>/Si substrate (Figure 5-1). The depths of trenches are varied from a flat substrate to  $d = 1600$  nm. The sample current was collected during deposition.

Before deposition, the pattern was aligned such that the pillars were deposited on the edge of the trenches as shown in Figure 5-1a and 5-1b. Edge effects are captured by the sample current trace at  $t = 0$  s, the instance of pillar formation. The slight decrease in  $i_s$  magnitude for all the deposits, except on the flat substrate (red trace in Figure 5-1), is a result of increased surface area at the edge of the trench, hence, an increase in electron scattering. This high sensitivity of the collected sample current makes it a robust data

stream for 3D FEBID. As the pillar deposition ensues,  $di_s/dt$  increases at the same rate for all the pillars and even at the transition.

$i_s$  decay at the segment phase, increases with increase in trench depth, where  $di_s/dt$  is increasingly negative the deeper the milled substrate goes, as shown in Figure 5-1d. Notably, the segment width (Figure 5-1a), vertical thickness, and  $\zeta$  (Figure 5-1b) remain constant for all the deposits including the one deposited on a flat substrate. This alludes to an intrinsic FEBID mechanism.

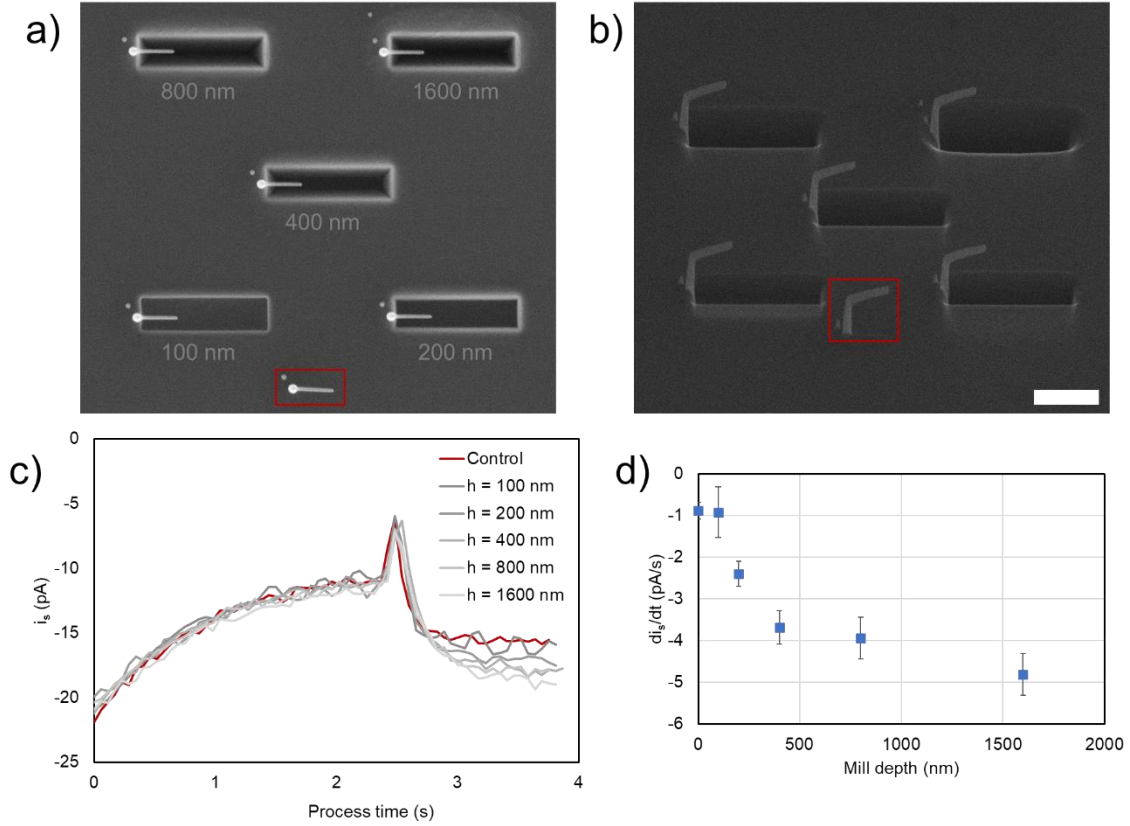


Figure 5-1 (a) Top down view SEM image of the SE capture experiments. The milled depths are notated on the image. A decrease in contrast of the milled trenches indicates increase in depth. (b) 52° tilted view of (a) showing the pillar aligned to the trench edge. The control calibration structure is deposited on un-milled substrate (red). (c) Collected sample current traces during deposition. (d) The  $i_s$  slopes ( $di_s/dt$ ) of the segment element showing variation with trench depth. For all the segments;  $\zeta = 30^\circ$ , pillar = 400 nm, segment = 400 nm. For the trenches; length = 1 mm, width = 250 nm. Scale bar = 500 nm.

## 5.5 A Sample Current Trace Artifact

per area Figure 4-8 shows ( $i_s$ ) profiles collected during the experimental deposition of calibration structures with a variable segment angle spanning  $12.5^\circ$  to  $80^\circ$ . The slopes,  $di_s/dt$  for the segment element sample current ( $i_s$ ) derived from Figure 4-8 are shown in Figure 5-2. Here, the general trend indicates that  $di_s/dt \rightarrow 0$  with increasing ( $\zeta$ ) and for higher electron energy. However, SE capture experiments (Figure 5-1) revealed that the ‘true’ segment deposit sample current decay,  $di_s/dt \ll 0$ .

What has remained unexplained, is the decay in the sample current trace during FEBID segment deposition. However, considering the discussion in the previous sections, the net effect is clear – a decrease in the deposition rate per pixel due to a reduction in thickness in the  $z$ -dimension. This was confirmed by secondary electron imaging, which revealed a steady decrease in the segment angle and segment  $z$ -thickness with increasing segment length (Figure 4-2). Electron beam induced heating is investigated as a plausible culprit for the decrease in growth rate which causes segment tapering and consequently sample current decay.

An analytical model of FEBID-induced heating is derived to estimate the range of temperatures expected to develop during FEBID, specifically, the maximum temperature at the beam impact region (BIR). Changes in temperature could significantly impact the mean precursor surface residence time ( $\tau$ ) on the deposit surface due to Arrhenius behavior. This phenomenon was recognized in 2006 [78] during FEBID studies using the precursor (hfac)CuVTMS where it was stated that; “The adsorbed amount of precursor per area

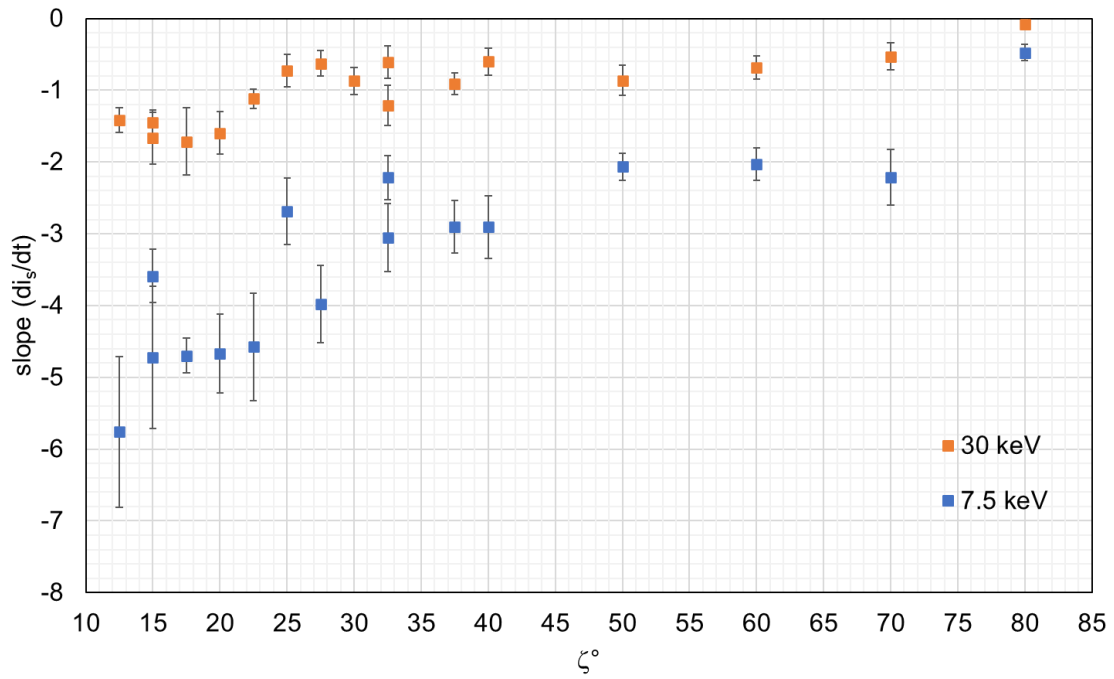


Figure 5-2 Sample current trace slopes calculated over segment growth for 30 keV and 7.5 keV data in represented in Figure 4-8. The error bars indicate the deviation from the average  $\Delta i_s/\Delta t$  calculated for each data point along a selected current trace.

decreases exponentially with increasing temperature due to increasing desorption.” [78]  
The derived 1D analytical model is now introduced. The assumptions and results provide an instructive guide to later interpret 3D beam heating results.

## 5.6 1D Beam Induced Heating Analysis

Beam heating effects during FEBID are estimated using a 1D analytical model based on the classical heat transfer problem of the extended cylinder. The pillar and segment are modeled collectively as a linear nanowire, for all  $\zeta$  spanning 0–90°. Therefore, it is required that the linear model implicitly account for the variation in the multidimensional segment angle.

Experiments show that the segment cross-sectional area varies with  $\zeta$ . Therefore, the segment angle effect is implicitly introduced into the model by measuring the segment cross-sectional area ( $A_s$ ) from experiments for use as an input parameter in the 1D model. The importance of ( $A_s$ ) during heat flow can be understood considering the thermal resistance;

$$R_T = \frac{L_T}{kA} \left[ \frac{K}{W} \right] \quad (5-3)$$

where ( $L_T$ ) is the total pathlength of the calibration structure, ( $k$ ) is the thermal conductivity and ( $A$ ) is the general cross-sectional area. A change in cross-sectional area versus the path length coordinate ( $s$ ) along the nanowire  $A(s)$  also must be included in the model

because the cross-sectional area of the pillar and segment are different under most deposition conditions.

The model was derived starting with the integration of Fourier's law separated in temperature (T) and pathlength (s);

$$q_b \int_0^{s=L_T} \frac{ds}{A(s)} = -k \int_{T_s}^{T_{BIR}} dT \quad (5-4)$$

where  $q_b$  is the incident beam heating rate and  $(T_s)$  is the substrate surface temperature.

This method can be used when

- (1) heat transfer is steady state,
- (2) energy is not generated in the volume of the object, and
- (3) heat loss via transfer across the surface area  $2\pi rL_T$  is negligible.

Importantly, the beam heating rate induced in the solid ( $q_b$ ) must be conserved at all points along the s-dimension, under steady-state conditions, and causes the temperature increase at  $(T_{BIR})$ . The full list of assumptions, model features and the rationale of their application is as follows.

- A constant cross-sectional area is applied to both the pillar ( $A_p$ ) and the segment ( $A_s$ ) elements. The average diameter is applied even though pillars deposited at 30 keV are known to taper with a sharp apex. The tapering is ignored in the model.

## Dimension Translation

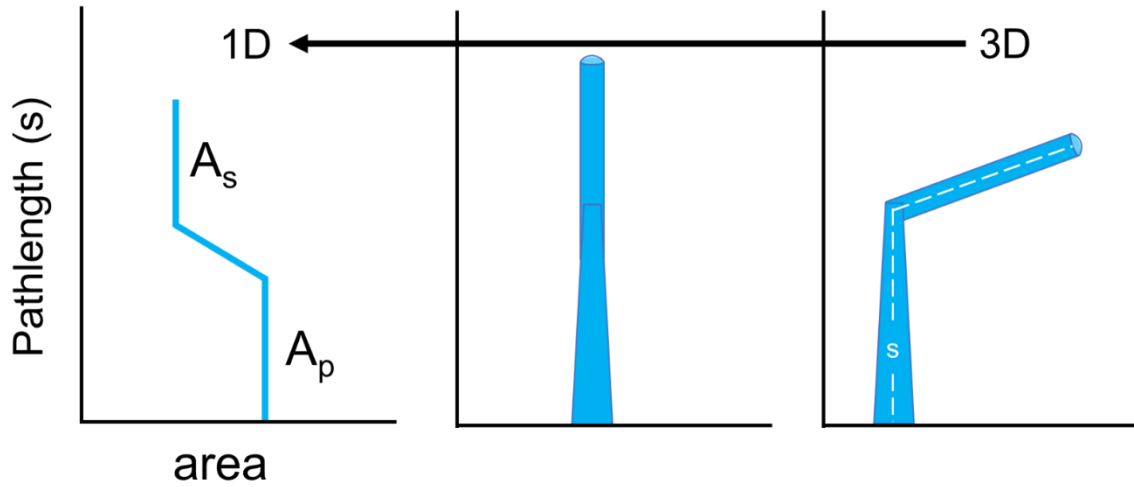


Figure 5-3 The segment angle ( $\zeta$ ) is implicitly included in the 1D beam heating model by using a cross-sectional area function  $A(s)$  that varies over the pathlength ( $s$ ) of the deposit. The influence of thermal resistance as a function of segment angle is thus included. The average cross-sectional area of the pillar element is  $A_p$  and  $A_s$  for the segment and are the critical parameters dictating the thermal resistance. For  $E_0 = 30$  keV and 32 pA,  $A_p = 2830 \text{ nm}^2$  and  $A_s(\zeta) = A_p(1 - e^{-\zeta/(30-0.2\zeta)})$ , where  $\zeta$  is in degrees.

- The general mathematical function  $\tanh(s)$  is used to describe the change in area upon the abrupt transition from the pillar to segment elements. Experiments show that the transition length ( $dL_{p-s}$ )  $\ll L_T$ , where  $L_T$  is the total calibration structure length (Figure 5-3).

$$A(s) = A_p + \left( \frac{A_s - A_p}{2} \right) \left( 1 + \tanh \left( \frac{s - L_p}{dL_{p-s}} \right) \right) \quad (5-5)$$

The transition length is related to the segment angle ( $\zeta$ ) and the pillar area according to  $dL_{p-s} = (A_p/\pi)^{1/2}/\cos(\zeta)$ .

- Thermal conduction was considered only along the pathlength ( $s$ ) of the calibration structure; radially oriented thermal gradients are ignored.
- The electron energy loss, or EEL, during primary electron transmission through the BIR provided the heating rate term ( $q_b$ );

$$q_b = f_U dE' \alpha(s) \frac{i_b}{q_e} \quad (5-6)$$

where ( $f_U$ ) is fraction of the inelastic energy transferred to the deposit as heat (Section 5.8), ( $dE'$ ) is the EEL per unit length of deposit [17] and  $\alpha(s)$  is the primary electron pathlength through the deposit. Inelastic energy is assumed to be lost continuously along the pathlength as Joule heating and therefore  $\alpha(s)$  is an absorption thickness. Details of the absorption thickness and the dependence on segment angle are discussed in Section 5.9.

- The substrate volume far exceeds the calibration structure volume. Thus, the substrate can easily accommodate an internal energy increase with a negligible temperature rise ( $T_{\text{sub}}$ ). Also, heat transfer at the substrate surface includes the effect of the thin 5 nm thermal  $\text{SiO}_2$  film upon which the deposit rests. The boundary condition at the  $\text{SiO}_2$ –deposit interface is;

$$-k_s \frac{dT}{ds} \big|_{\text{SiO}_2} = -k \frac{dT}{ds} \big|_{\text{PtC}_5} \quad (5-7)$$

where ( $k_s$ ) is the thermal conductivity of  $\text{SiO}_2$ . In Section 5.12 the temperature at the deposit- $\text{SiO}_2$  boundary is derived by the finite difference approximation.

- Each solution of Equation 5-4 for  $T_{\text{BIR}}$  in the range  $s = 0: \Delta L:L_T$ , can be collectively viewed as the actual BIR temperature because the beam speed is extremely slow relative the thermal diffusion rate. As a result, steady–state conditions develop quickly after the beam is displaced. The modified Peclet number verifies this assumption;

$$Pe = \frac{vL}{\alpha_T} = Pe_{\text{FEBID}} = \frac{\left(\frac{\Delta}{\tau_d}\right) L_T}{\left(\frac{k}{\rho c_p}\right)} \quad (5-8)$$

where the numerator is an advection–like term that, in this instance, accounts for beam motion while the denominator is a thermal diffusivity ( $\alpha_T$ ).  $Pe = 10^{-6}$  for  $L_T = 10^3$  nm and an electron beam speed of  $v = 10^2$  nm/s. This very small value for (Pe) indicates

that steady-state heat transfer is established along the length of deposit during 3D FEBID quickly after beam translation to a new dwell position on the deposit because the patterning velocity is very slow relative to the thermal diffusivity.

Finally, the integration of Equation 5-4, with the application of the boundary conditions, gives;

$$T_{max} = T_{sub} + \frac{q_b h_s}{k_s L_T} G + \frac{q_b}{k} G \quad (5-9)$$

where (G) is a geometry dependent function and is provided in Section 5.10.

## 5.7 Characteristics of Beam-Induced Heating via 1D Model

The 1D beam heating model reveals several important characteristics of beam-induced heating. Figure 5-4 shows the predicted BIR temperature versus total deposit height in the z-coordinate for  $\zeta = 12.5^\circ\text{--}50^\circ$ . (z) is used in the abscissa used for two reasons. First, deposition time does not appear explicitly in the 1D model. Second, the bottom-up nature of 3D nanoprinting makes (z) the critical parameter for unraveling heat evolution as a 3D structure grows. For this reason, the spatial derivative (dT/dz) is an important quantity for discussing thermal effects in 3D FEBID nanostructures. The most significant results in Figure 5-4 are now discussed.

### *Pillar stage*

The 1D model predicts a linear rise of temperature during pillar deposition stage (Figure 5-4). The beam heating rate ( $q_b$ ) is independent of pillar height due to the assumption of a constant beam absorption thickness. Thus, the increase in temperature is solely due to the increase in the thermal resistance caused by the increase in the pillar length.

### *Transition stage*

The transition stage is characterized by a significant reduction in temperature; a reduction which is more pronounced for smaller segment angles. The general temperature reduction observed for all segment angles is due to the abrupt change in adsorption thickness when the beam irradiation geometry switches from para-axial to trans-axial with respect to the deposit growth direction. The absorption thickness transitions from the relatively long pillar to the thin segment nuclei.

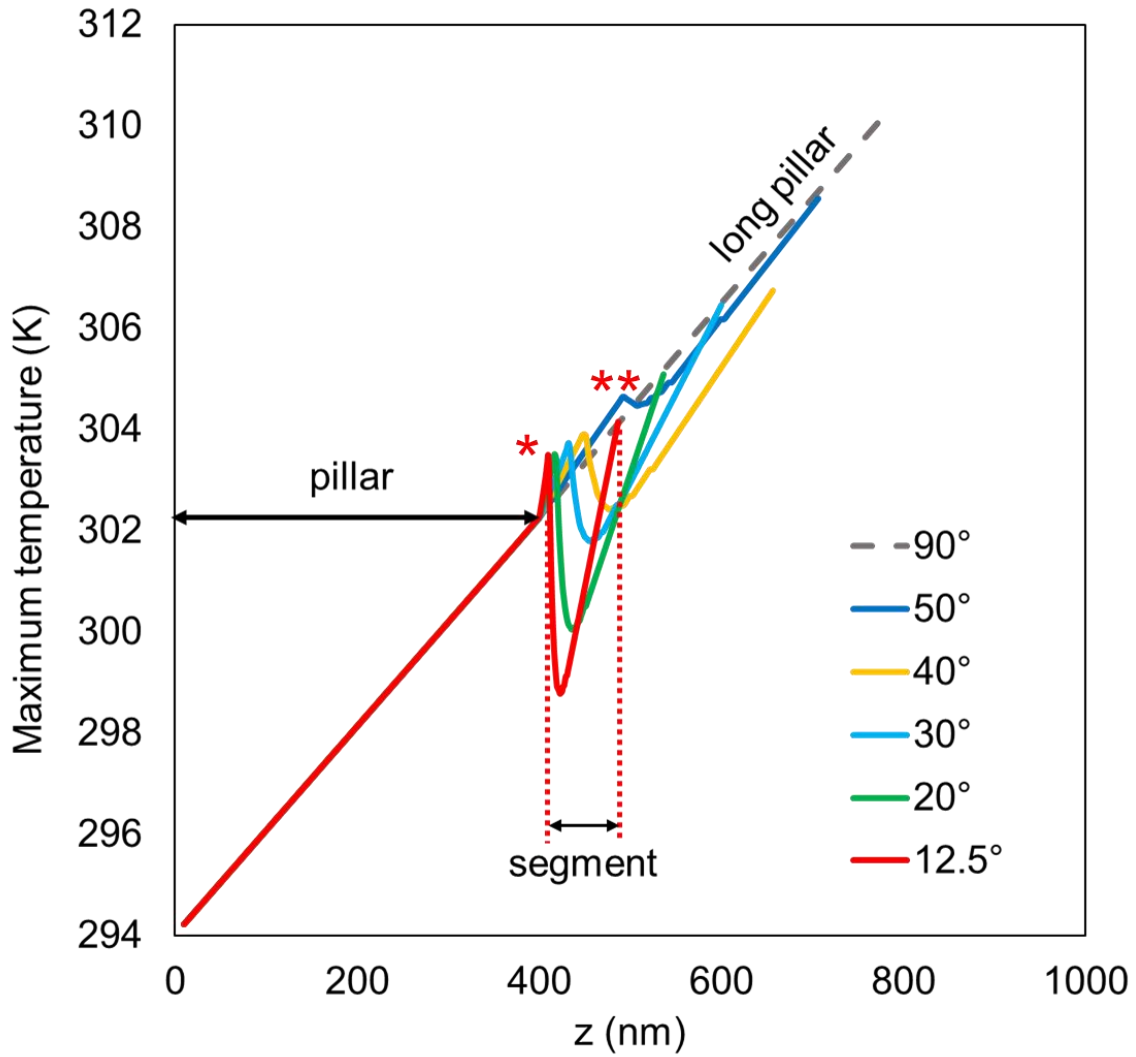


Figure 5-4 The maximum temperature of the deposit as a function of the total deposit height along the  $z$ -coordinate predicted by the 1D mathematical model for  $E_o = 30$  keV and  $i_b = 32$  pA. The maximum temperature always occurs at the beam-impact region, or BIR. For the  $\zeta = 12.5^\circ$  case; (\*) indicates the transition stage between pillar and segment growth and (\*\*) shows the completion of deposition.

The segment angle dependence of the temperature decrease is ultimately caused by the reduced VGR, a consequence of a relatively faster  $v_b$ . The dose per unit length  $i_b/(q_e v_b)$  is thus lower yielding less deposition per unit length and a relatively low vertical growth rate (VGR). Thus, the initial segment nuclei are relatively small for large  $v_b$ . As a result, the quantity of absorbed internal energy per incident electron is lower at lower ( $\zeta$ ). This reduces the absorption thickness for the next pixel point propagating the effect via positive feedback.

### *Segment stage*

The final BIR temperature and the change in BIR temperature with segment length ( $\Delta T/\Delta s$ ) both vary with segment angle. These observations together characterize the heating situation in the segment stage.

The final BIR temperature, measured at the final segment length of 400 nm, increases progressively with ( $\zeta$ ) due simply to the increase in absorption thickness. The source term ( $q_b$ ) magnitude increases with ( $\zeta$ ) as a result (see Equation 5-6).

The impact of the thermal resistance ( $R_T$ ) on segment heating is revealed by plotting the BIR temperature as a function of segment pathlength along the calibration element ( $s$ ). Figure 5-5a shows ( $T$ ) versus ( $s$ ) trajectories ranging from 12.5° to 50°. ( $\Delta T/\Delta s$ ) is the change in BIR maximum temperature per unit length of new deposit formed. ( $\Delta T/\Delta s$ ) is derived from these plots and is shown in Figure 5-5b. The temperature ( $T$ ) versus displacement ( $s$ ) plots shown in Figure 5-5a are derived by solving Equation 5-4 for each data point constituting the curve. Each point is calculated as a steady-state solution to the

problem that yields the maximum BIR temperature. In Figure 5-5b, the slope of each curve has been taken as representative of the change in BIR temperature as a function of segment length, or  $\Delta T/\Delta s$ . This is not to be confused with  $dT/ds$  which would represent the temperature gradient as a function of length of segment. The plot shows  $(\Delta T/\Delta s)$  as a function of  $\zeta$  derived from the 1D heat model.

$(\Delta T/\Delta s)$  exhibits a minimum value at a  $\zeta \sim 30^\circ$  (Figure 5-5b). At lower  $\zeta$ ,  $R_T$  increases due the smaller segment cross-sectional area. The increase in  $R_T$  leads to an increase in the BIR temperature per unit segment pathlength. As a result, below  $\zeta \sim 30^\circ$  an increase in  $(\Delta T/\Delta s)$  is observed with decreasing segment angle. Beyond  $30^\circ$ , the electron beam source term ( $q_b$ ) dominates heat transport, again, due to the increasing absorption thickness. The source term overwhelms the increase in thermal conductance even though  $R_T$  is decreasing with increasing segment angle.

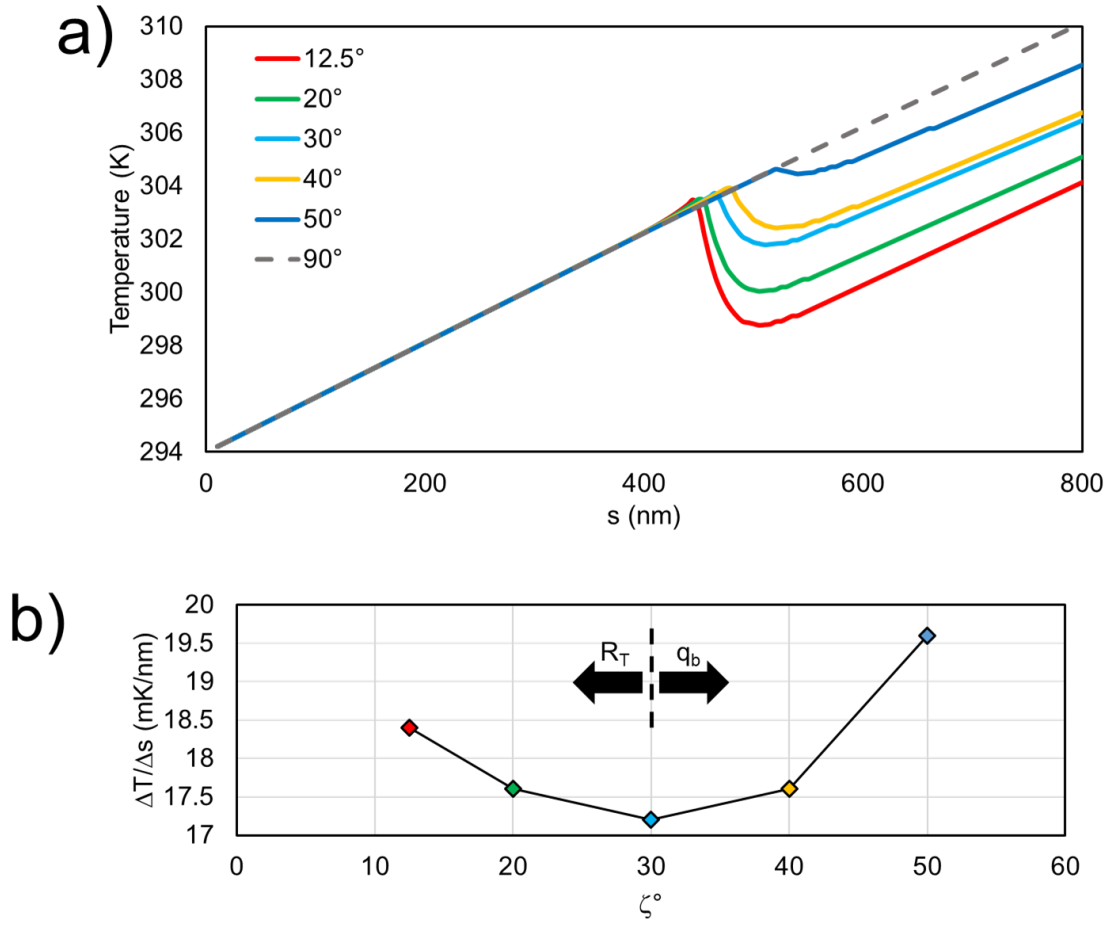


Figure 5-5 (a) 1D beam heating model predictions of the BIR temperature versus pathlength ( $s$ ) along the deposit. The slope of these curves (b) in the segment growth stage,  $s > 400$  nm shows the relative influence of the thermal resistance ( $R_T$ ) and the beam induced heating rate ( $q_b$ ). The color of each data point is referenced to each segment based on the segment angle ( $\zeta$ ).

## 5.8 Heat Transfer from Inelastic Energy Loss

The fraction of inelastic energy ( $f_U$ ) that is released to the solid as internal energy during the primary electron–deposit interaction is;

$$f_U = (1 - f_{SE}) + f_{SE} \left( \frac{\bar{\varepsilon} - E_{SE}}{\bar{\varepsilon}} \right) \quad (5-10)$$

( $f_{SE} = 0.60$ ) is the fraction of inelastic energy that is allocated for SE creation in the model, and later used in the 3D FEBID simulation. It is assumed that the remainder of the inelastic energy ( $1 - f_{SE}$ ) is transferred to the deposit as internal energy. This is an overestimation considering that there are other channels for energy loss, e.g., x-ray production, in the solid. However, these are known to be small in comparison with the Joule heating component. An additional source of internal energy must also be considered which is the waste energy resulting from SE creation.

The energy required to create an SE in the carbon phase is  $\varepsilon_C = 80$  eV while in the platinum phase  $\varepsilon_{Pt} = 30$  eV [17]. In the full 3D FEBID simulation, each SE created has the average energy of  $E_{SE} = 19$  eV for PtC<sub>5</sub>. This model of SE energy is also applied to the 1D model. Therefore, in both the 1D model and 3D simulation it is assumed that the by-product energy from SE creation is also absorbed by the solid. The development of this energy term requires consideration of the deposit composition and nanostructure. The nanostructure is a mixture of platinum nanoparticles [74] embedded in a hydrogenated amorphous carbon matrix [79]. The average energy required to create an SE ( $\underline{\varepsilon}$ ) is used to include the influence of the nanostructure;

$$\bar{\epsilon} = V_{Pt}\epsilon_{Pt} + V_C\epsilon_C \quad (5-11)$$

where  $V_{\text{phase}}$  represents the volume percent of each material phase in the deposit.

The fraction of internal energy absorbed by the deposit during SE creation is proportional to both ( $f_{SE}$ ), but also the energy difference between the average energy required to create the SE ( $\bar{\epsilon}$ ) and the actual SE energy ( $E_{SE}$ ), or;

$$f_{SE} \left( \frac{\bar{\epsilon} - E_{SE}}{\bar{\epsilon}} \right)$$

This is the second term in Equation 5-10.

## 5.9 The Absorption Thicknesses

Heating model calculations were executed for calibration structure deposits that were grown using a primary electron beam energy of  $E_o = 30$  keV. At this relatively high beam energy, the total electron energy transferred to the segment is small because the segment thickness along the penetration path ( $\Delta z$ ), is small, on the order of  $10^2$  nm. Thus, at  $E_o = 30$  keV,  $\Delta z \ll R_e$  where  $R_e$  is the electron penetration range. As a result, the energy of the primary electron beam at all points along the pathlength through the solid is taken simply as ( $E_o$ ). The inelastic electron energy loss rate ( $dE'$ ) is a function of ( $E_o$ ). Thus, ( $dE'$ ) in Equation 5-6 is also constant, regardless of the segment thickness. A value of  $dE' = 2.54$  eV/nm was calculated using the Bethe, Joy and Luo expression [80].

The primary electron absorption thickness  $\alpha(S)$  exhibits a transition from the pillar to segment growth stages according to;

$$\alpha(S) = \alpha_p + \left( \frac{\alpha_s(\zeta) - \alpha_p}{2} \right) \left( 1 + \tanh \left( \frac{S - L_p}{dL_{p-s}} \right) \right) \quad (5-12)$$

The primary electron absorption thickness  $\alpha(S)$  is estimated in two different ways for the pillar and segment growth phases. ( $\alpha_p$ ) is assumed to be constant for the entire pillar growth phase, independent of the height of the pillar. During the segment growth phase,  $\alpha_s(\zeta)$  is set as equal to the segment thickness ( $\Delta z$ ) and derived from real experiments. This parameter varies with segment angle  $\alpha_s(\zeta)$ . The assumption of  $\alpha_s(\zeta) = \Delta z$  is based on the low elastic scattering probability for a relatively high energy primary electron ( $E_o = 30$  keV) during transmission through a relatively thin specimen ( $\Delta z \sim 10^2$  nm) – negligible primary electron deflection is anticipated.

The transition length in Equation 5-12 is derived from experimental parameters and is defined as the distance along the pathlength of the deposit over which the pillar is transforming into a segment. Specifically, ( $dL_{p-s}$ ) is proportional to the cross-sectional area of the pillar ( $A_p$ ) and the segment angle;

$$dL_{p-s} = \frac{r_p}{\cos \zeta} = \frac{\sqrt{A_p}}{\sqrt{\pi} \cos \zeta} \quad (5-13)$$

The electron beam must move a distance ( $r_p$ ), starting from the pillar center axis, to fully transition from pillar to segment growth. In real experiments, the pillar radius ( $\sim 30$  nm) is much larger than the digital beam pitch (1 nm). Thus, as segment growth ensues, the beam irradiates both the segment and pillar over ( $dL_{p-s}$ ).

## 5.10 Cross-Sectional Area Variation

Integration of Fourier's Law applied to the 1D heat transfer problem with the area variation term (Equation 5-4) yields the following geometric factor (G).

$$G = \frac{dL_{p-s}(A_p - A_s) \ln \left[ (A_s - A_p) \sinh \left( \frac{s - L_p}{dL_{p-s}} \right) + (A_p + A_s) \cosh \left( \frac{s - L_p}{dL_{p-s}} \right) \right] + (A_p + A_s)(s - L_p)}{2A_p A_s} \Bigg|_0^s \quad (5-14)$$

The factor (G) depends exclusively on the FEBID calibration structure geometry. Finally, the substrate surface temperature is related the substrate temperature using the flux balance at the surface–deposit interface which includes the effect of the thin 5 nm thermal SiO<sub>2</sub> film ( $h_s$ ) upon which the deposit rests. Thus, the boundary condition at the SiO<sub>2</sub>–deposit interface is;

$$-k_s \frac{dT}{ds} \Big|_{SiO_2} = -k \frac{dT}{ds} \Big|_{PtC_5} \quad (5-15)$$

where ( $k_s$ ) is the thermal conductivity of SiO<sub>2</sub>. The thermal conductivity of the supporting thermal silicon dioxide ( $k_s = 1.3$  [W/m/K]) is much greater than the thermal conductivity determined for the deposit ( $k = 0.16$  [W/m/K]). Therefore, the deposit is the dominating thermal resistance in the deposit/substrate couple. As a result, the presence of the thermal silicon dioxide film has a negligible impact on heat transport.

Finally, the indefinite integration (Appendix A) of Equation 5-4, with the application of the boundary conditions, gives;

$$T(s) = T_{sub} + \frac{q_b(S)}{k_s} \frac{h_s}{S} G(s) + \frac{q_b(S)}{k} G(s) \quad (5-16)$$

The definite integration (Appendix B) result by substituting (S) for (s) in Equation 5-14, or;

$$T_{max}(S) = T_{sub} + \frac{q_b(S)}{k_s} \frac{h_s}{S} G(S) + \frac{q_b(S)}{k} G(S) \quad (5-17)$$

## 5.11 Temperature Dependent Properties

The 1D analytical model estimates that a significant change in the mean precursor surface residence time  $\tau(T)$  should be expected during FEBID based on the predicted BIR temperatures. This is estimated based on the activation energy [81] and pre-exponential [82] parameters reported for physisorption of the  $\text{MeCpPt}^{\text{IV}}\text{Me}_3$  molecule and an  $\text{SiO}_2$  surface.

Figure 5-6 (-) shows  $\tau(T)$  predicted for the  $\text{MeCpPt}^{\text{IV}}\text{Me}_3\text{--SiO}_2$  interface using the reported activation energy of  $E_a = 669 \text{ meV}$  [81] and the estimated pre-exponential attempt frequency  $k_0 \approx 1 \times 10^{13} \text{ Hz}$  applicable in the limit of the large molecule approximation [82]. For a temperature change predicted by the 1D heating model  $\Delta T \sim 10 \text{ K}$ , a decrease in  $\tau(T)$  exceeding 50% is expected. The implications of the temperature-dependent

behavior of the Pt precursor and its participation in FEBID reported by Cullen/Toth [83, 84] aided in the development and ultimately the exploration of the beam heating effect [84]. Utke [75] identified importance of considering  $\tau(T)$  while Randolph also identified the importance of  $\tau(T)$  during TEOS deposition using FEBID [56].

The 1D model of beam heating predicts significant impact of the BIR temperature rise on 3D FEBID. The thermal conductivity of the deposit ( $k$ ), the activation energy for physical desorption of precursor from the deposit surface ( $E_a$ ) and the fraction of inelastic energy deposited that contributes to Joule heating ( $f_U$ ) were modulated to match experimental results with simulations because these values are unknown for the  $\text{PtC}_5$  deposit. ( $k$ ) was assumed to be dominated by the amorphous carbon phase and was restricted to the range of 0.1–1 [85, 86] when searching for simulations that reproduced experiments. The activation energy was varied over the range of 100 meV, centered on the value reported for the  $\text{MeCpPt}^{\text{IV}}\text{Me}_3\text{--SiO}_2$  interaction above (669 meV). ( $f_U$ ) was varied from 0.50–1 as it is well known that a significant amount of electron energy loss yields Joule heating [62].

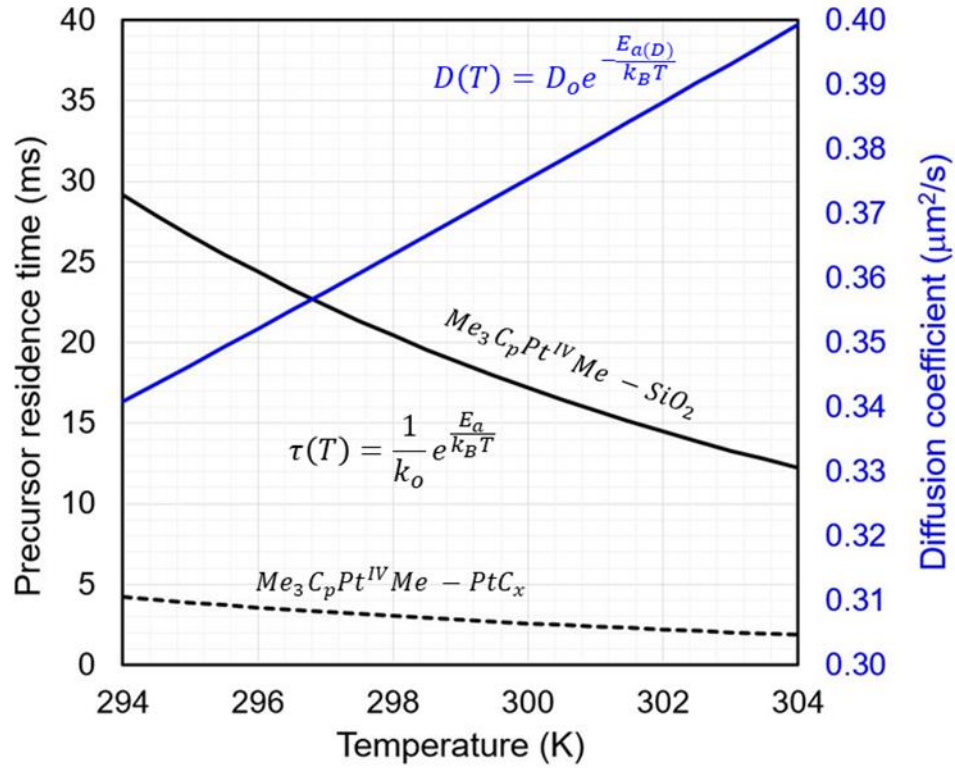


Figure 5-6 (-) The temperature-dependent surface residence time  $\tau(T)$  of  $\text{MeCpPt}^{\text{IV}}\text{Me}_3$  on  $\text{SiO}_2$  [75].  $k_0 = 1013 \text{ Hz}$  and  $E_a = 669 \text{ meV}$ . Based on simulations  $\tau(T)$  is updated for the  $\text{MeCpPt}^{\text{IV}}\text{Me}_3$ – $\text{PtC}_x$  interface which controls 3D FEBID [74].  $E_a$  is updated to a value of  $0.62 \text{ eV}$  (--) that produced simulation results which predicted 3D FEBID experiments. It is estimated to be the  $E_a$  for the  $\text{MeCpPt}^{\text{IV}}\text{Me}_3$ – $\text{PtC}_x$  interface. In comparison to  $\tau(T)$ , surface diffusion  $D(T)$  is less sensitive to temperature changes (-) [76].  $D_0 = 42 \text{ mm}^2/\text{s}$  and  $E_{a(D)} = 122 \text{ meV}$ .

### 5.12 Finite Difference Approximation at Deposit-Substrate Boundary

Prior to the development of the 1D beam heating analytical model presented above, heating effects were absent in a 3D numerical simulation currently used to emulate 3D nanoprinting using EBID. Considering the results of the 1D analytical model, it was determined that the 3D heating equation must be solved in tandem with the rate equations to incorporate heating effects during EBID toward a more accurate description of the deposition rate. As part of this integration, a boundary condition was required to account for the change in thermal conductivity across the thin and insulating silicon dioxide layer present between the silicon substrate and the composite PtC<sub>5</sub> deposit. An implicit finite difference method was ultimately used to numerically predict heat flow. The following derivation shows the form of the Taylor approximation used at the deposit voxel boundary, adjacent to the insulating boundary, as well as the heating rate balance at the substrate – oxide interface required to calculate the temperature ( $T_w$ ). These contributions helped upgrade the current 3D numerical simulation of EBID to incorporate Joule heating effects into final computer predictions.

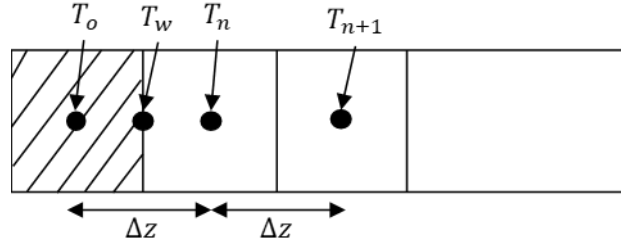


Figure 5-7 A schematic representing the Taylor series expansion variables and coefficients

Taylor series expansion about  $T_n$  is given as:

$$T_{n+1} = T_n + \Delta z \frac{dT}{dz} + \frac{\Delta z^2}{2!} \frac{d^2T}{dz^2} + \frac{\Delta z^3}{3!} \frac{d^3T}{dz^3} + \dots \quad (5-18)$$

$$T_w = T_n - \frac{\Delta z}{2} \frac{dT}{dz} + \frac{\left(\frac{\Delta z}{2}\right)^2}{2!} \frac{d^2T}{dz^2} - \frac{\left(\frac{\Delta z}{2}\right)^3}{3!} \frac{d^3T}{dz^3} + \dots \quad (5-19)$$

Simple arithmetic gives,

$$T_{n+1} = T_n + \Delta z \frac{dT}{dz} + \frac{\Delta z^2}{2} \frac{d^2T}{dz^2} + \frac{\Delta z^3}{6} \frac{d^3T}{dz^3} + \dots \quad (5-20)$$

$$T_w = T_n - \frac{\Delta z}{2} \frac{dT}{dz} + \frac{\Delta z^2}{8} \frac{d^2T}{dz^2} - \frac{\Delta z^3}{48} \frac{d^3T}{dz^3} + \dots \quad (5-21)$$

Since we want an approximation of the second derivative, multiply (5-20) by A and (5-21) by B and add. Then set the coefficients of first and third derivative to zero and second derivative to 1. This gives two equations with two unknowns.

$$A \left[ T_{n+1} = T_n + \Delta z \frac{dT}{dz} + \frac{\Delta z^2}{2} \frac{d^2T}{dz^2} + \frac{\Delta z^3}{6} \frac{d^3T}{dz^3} + \dots \right] \quad (5-22)$$

$$B \left[ T_w = T_n - \frac{\Delta z}{2} \frac{dT}{dz} + \frac{\Delta z^2}{8} \frac{d^2T}{dz^2} - \frac{\Delta z^3}{48} \frac{d^3T}{dz^3} + \dots \right] \quad (5-23)$$

Simple algebra gives,

$$AT_{n+1} = AT_n + \Delta z A \frac{dT}{dz} + \frac{\Delta z^2}{2} A \frac{d^2T}{dz^2} + \frac{\Delta z^3}{6} A \frac{d^3T}{dz^3} + \dots \quad (5-24)$$

$$BT_w = BT_n - \frac{\Delta z}{2} B \frac{dT}{dz} + \frac{\Delta z^2}{8} B \frac{d^2T}{dz^2} - \frac{\Delta z^3}{48} B \frac{d^3T}{dz^3} + \dots \quad (5-25)$$

$$\begin{aligned} AT_{n+1} + BT_w &= (A + B)T_n + \left( \Delta z A - \frac{\Delta z}{2} B \right) \frac{dT}{dz} \\ &+ \left( \frac{\Delta z^2}{2} A + \frac{\Delta z^2}{8} B \right) \frac{d^2T}{dz^2} + \left( \frac{\Delta z^3}{6} A - \frac{\Delta z^3}{48} B \right) \frac{d^3T}{dz^3} \end{aligned} \quad (5-26)$$

Setting the first and second derivative coefficients to 0 and 1 respectively we get,

$$\Delta z A - \frac{\Delta z}{2} B = 0 \rightarrow 2A = B \quad (5-27)$$

$$\frac{\Delta z^2}{2}A + \frac{\Delta z^2}{8}B = 1 \quad (5-28)$$

$$A = \frac{4}{3\Delta z^2}; B = \frac{8}{3\Delta z^2} \quad (5-29)$$

Substituting A and B in Equation 5-26,

$$\frac{4}{3\Delta z^2}T_{n+1} + \frac{8}{3\Delta z^2}T_w = \left(\frac{4}{3\Delta z^2} + \frac{8}{3\Delta z^2}\right)T_n + \frac{d^2T}{dz^2} \quad (5-30)$$

$$\frac{d^2T}{dz^2} = \frac{8T_w - 12T_n + 4T_{n+1}}{3\Delta z^2} \quad (5-31)$$

To solve for  $T_w$ ,

$$-k_s \frac{dT}{dz} \big|_{LHS} = -k \frac{dT}{dz} \big|_{RHS} \quad (5-32)$$

$$-k_s \frac{(T_w - T_o)}{\frac{\Delta z}{2}} = -k \frac{(T_n - T_w)}{\frac{\Delta z}{2}} \quad (5-33)$$

$$T_w = \frac{k_s T_o + k T_n}{k + k_s} \quad (5-34)$$

### 5.13 3D FEBID Simulations Confirm Heating Results

3D FEBID simulation allows for selective manipulation of physical parameters that influence FEBID process. The ability to switch parameters on or off helps to show the effect of a single parameter involved in a complex multi-parameter interaction. Thus, it is a powerful method that clarifies an otherwise complex deposition process.

For this discussion, the precursor surface concentration,  $C(x,y,z,t)$  on the deposit will be controlled;

$$\frac{\partial C}{\partial t} = D(T)\nabla^2 C + \nabla D(T)\nabla C + \frac{\delta\Phi}{s_p}(s_p - C) - \frac{C}{\tau(T)} - \sigma C i_{SE} \quad (5-35)$$

where  $(\delta)$  is the precursor sticking probability,  $(\Phi)$  is the precursor vapor phase impingement flux,  $(s_p)$  is the monolayer precursor surface concentration,  $(\sigma)$  is mean electron impact precursor dissociation cross-section and  $(i_{SE})$  is the secondary electron current density 3D profile. The first two terms on the right-hand side of Equation 5-35 define precursor transport by surface diffusion, the third term is the precursor attachment flux, the fourth term accounts for the precursor desorption flux, and lastly, the fifth term is SE precursor dissociation.

Joule heating,  $q_b$  effects for low segments angles produce structures with the most noticeable deflection and are therefore the most suitable for maximizing beam heating characteristics. Therefore, a low segment angle ( $\zeta = 15^\circ$ ) is used to compute the reaction kinetics for the 3D FEBID simulations shown in Figure 5-8.

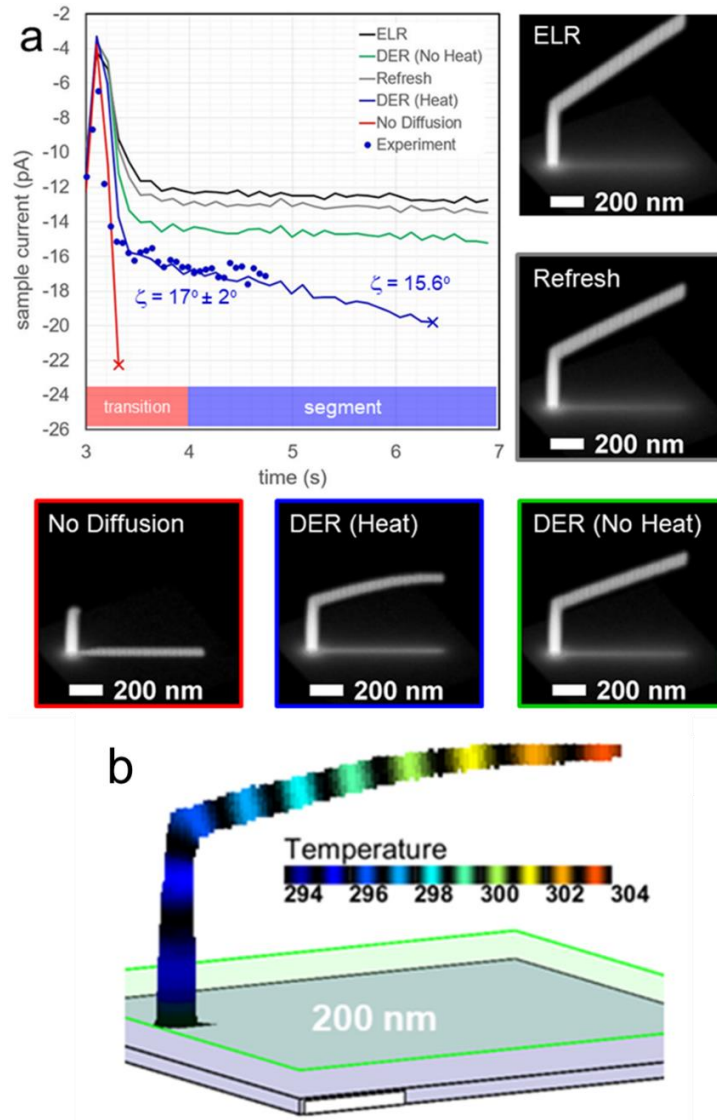


Figure 5-8 (a) Sample current traces for the calibration structure *transition* and *segment* at  $E_0 = 30$  keV and  $i_b = 32$  pA under the following simulated conditions: electron-limited 'ELR', precursor-limited 'Refresh', diffusion-enhanced 'DER' regimes, no surface diffusion 'No Diffusion', and electron beam heating 'DER (Heat)'. An experimental data set for a complementary calibration structure ( $\bullet$ ) is provided for reference.  $\zeta = 17^\circ$  for the experiment and  $\zeta = 15.6^\circ$  for the simulation. (b) Temperature map for the 'DER (Heat)' with beam heating applied at the BIR. Pillar = 400 nm and segment = 800 nm.

### 5.13.1 Electron-Limited Regime (ELR)

Simulated ELR conditions were obtained by constraining the surface precursor coverage to an equilibrium value ( $C_0 = 2$  molecules/nm<sup>2</sup>), regardless of the rate of precursor consumption in the BIR. The steady-state surface precursor coverage value is established by the balance between the precursor attachment flux and the surface desorption flux. Beam induced heating is not initiated for the ELR simulation condition. The resulting sample current along with the virtual SEM of the final calibration structure is presented in Figure 5-8a. This setting has the highest sample current during segment growth with the maximum final deposit height and  $\zeta$ , (ELR inset) compared to the other simulated conditions. The segment is linear and without deflection/bending, and yet  $di_s/dt < 0$ . It is expected that a constant ( $\zeta$ ) should result in a constant ( $i_s$ ), however, the finite simulation domain size confines  $di_s/dt < 0$  affecting electron counting during the Monte Carlo simulation.

### 5.13.2 Precursor-Limited Regime (Refresh)

The impact of precursor depletion during only the beam dwell period can be achieved by forcing the surface precursor coverage back to an equilibrium value at the end of each beam dwell (Figure 5-8a grey line). When the beam is on, the precursor surface coverage naturally evolves as prescribed by Equation 5-35, only that a constant mean precursor surface residence time,  $\tau(T) = 4.22$  ms is maintained at room temperature (294 K). In this case, the simulation mimics an infinitely long precursor replenishment period between beam dwells, thus the term ‘Refresh’ is used to describe this simulation condition.

The absolute value of ( $i_s$ ) decreases relative to the ELR sample current trace which points to a decrease in deposit volume and is consistent with precursor depletion. In this case, the reaction kinetics has been switched to a precursor limited condition from ELR. Once again, a linear segment is generated as shown by the virtual SEM image and  $di_s/dt \approx 0$ .

### 5.13.3 Diffusion-Enhanced Regime (DER)

For this condition, the surface coverage evolves as it would during experiments at all processing times (Figure 5-8a green line). Hence, DER conditions develop as continuous segment growth needs the diffusion of surface bound precursor down the concentration gradient to the BIR [45]. Beam heating was not applied to this simulation condition. The DER case closely mimics reality and captures all the features of the sample current profile, relative to experiments (Figure 5-8a, ●), but for the segment deflection and the concurrent decay in sample current observed during experimental segment deposition ( $di_s/dt < 0$ ).

### 5.13.4 DER with Active Beam Induced Heating

The most realistic sample current simulation condition is represented with a solid blue line in Figure 5-8a. Beam induced heating was switched on during this simulation. Segment deflection is captured by the decay in sample current during the segment growth stage. Figure 5-8b shows the 3D temperature profile for the deposit surface for this simulation condition. The temperature gradient ( $dT/ds$ ) causes a decrease in the precursor reservoir along the segment that feeds the diffusion flux to the BIR, directly through the

term  $C/\tau(T)$  in Equation 5-35. Therefore,  $(C)$  is reduced along the calibration element axis toward the BIR.

#### **5.13.5 Reduced Diffusion Coefficient**

3D FEBID experiments and simulations are dictated by the diffusion-enhanced regime [18, 45]. The DER condition is seen to still dictate shape evolution even with beam induced heating included. However, in a simulation case where the magnitude of the diffusion coefficient is reduced, segment deposition fails. This is represented as No Diffusion in Figure 5-8a. 3D FEBID is impossible under this condition.

#### **5.14 Heat Compensation**

Insight into electron beam induced heating during FEBID through the 1D beam heating model and confirmation by simulations, makes it possible to overcome segment deflection by heat compensation. The 1D heating model revealed that the temperature dependent precursor residence time,  $\tau(T)$  varies the precursor surface concentration at the beam impact region. This concentration variation leads to segment tapering and deflection. In order to achieve linear segments, heat compensation aims to counteract the continuous decrease in concentration by continuously reducing the beam patterning speed,  $v_b$  by maintaining a constant pixel point pitch ( $\Lambda$ ) and increasing the pixel dwell time ( $\tau_d$ ) [87].

The increase in dwell time per pixel results in constant vertical growth rate for each pixel. This corrects the segment deflection and maintains a constant segment thickness with

elongation. The segment cross-section (Figure 5-9a and 5-9b inset) at the BIR increases by 13% for the heat compensated segment. As a result, SE emission is also constant along the corrected segment and  $di_s/dt = 0$  (Figure 5-9d). Consequently, this compensation strategy leads to higher in temperatures compared to uncompensated segments (Figure 5-9c). Without compensation, the segment vertical growth rate decreases with segment elongation thus reducing magnitude of the heating source term  $q_b$ . However, the higher temperatures during heat compensation are anticipated by the increasing dwell time resulting in linear segments.

The simulated non-linear segment, in Figure 5-9a is deposited at a constant dwell time,  $\tau_d = 8.20$  ms. To compensate for beam heating, the dwell time required to grow a linear segment with a constant segment thickness varies from  $\tau_d = 8.20$  to  $\tau_d = 13.10$  ms. The longer and dynamic dwell time per pixel increases the total processing time by 1.4 s as shown in Figure 5-9d. In general, 3D FEBID is a slower process compared to other 3D nanoprinting technologies [88]. However, it can be argued that the precision achieved with the additional deposition time is favorable compared the increased refresh time approach. In this alternative approach, the beam is periodically blanked to allow for intermittent cooling. Unfortunately, beam heating is an inevitable intrinsic process. The time it takes for heat transfer to reach steady is on the order of  $10^{-7}$  s while the total deposition and refresh times per pixel are on the order of  $10^{-3}$  s, therefore the electron beam would have to be turned off  $10^4$  times per pixel to deposit at a low temperature.

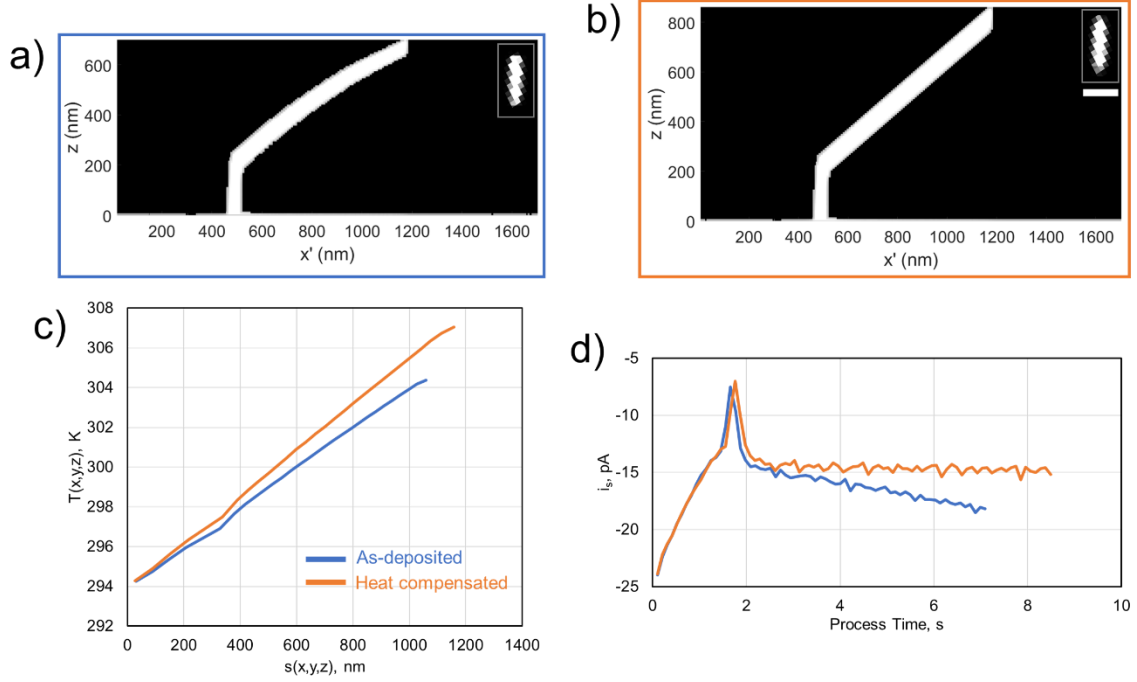


Figure 5-9 (a) 3D-FEBID virtual SEM image of a simulated as-deposited calibration structure exhibiting tapering and deflection. The dwell time per pixel  $\tau_d = 8.20$  ms for segment deposition,  $E_0 = 30$  keV,  $i_b = 32$  pA. (b) A complementary heat compensated calibration structure deposited with varying dwell times,  $\tau_d = 8.20 - 13.10$  ms. (c) Temperature plot along the deposit axis of (a)-blue and (b)-orange. (d) Sample current trace during deposition of (a) and (b). Inset: Segment cross-section virtual image viewed parallel to  $s(x, y, z)$  calibration structure axis. Pillar length = 200 nm, segment length = 800 nm and a segment angle of  $\zeta = 30^\circ$ . Inset scale bar = 50 nm.

## Chapter 6: Conclusion and Future work

Evolution of focused electron beam induced deposition (FEBID) from carbonaceous contamination to a versatile 3D-nanoprinting technology has been presented here. The direct write capability of complex 3D nanostructures with low restrictions on the substrate material and morphology, and access to a variety of deposit material are some of the advantages of 3D FEBID. However, the ability to precisely replicate original digital design in experiments and simulation precision is limited. Empirical corrections are required to compensate for nanowire distortion during deposition. This limits the nanoscale precision.

Investigations carried out through a combination of various experimental data streams at different electron beam energies, analytical models and simulations for 3D deposits using the  $\text{MeCpPt}^{\text{IV}}\text{Me}_3$  precursor, have revealed beam induced heating as the mechanism that causes loss of precision in 3D nanoprinting using FEBID.

The analytical models and simulations of heat flow predicted that a 10 K temperature increase at the beam impact region (BIR) reduces the precursor surface residence time by more than 50%. This produces a steady decrease of the nanowire vertical growth rate over process time. An observed increase in the temperature-dependent surface diffusion rate is not enough to compensate for the overwhelming loss of precursor by enhanced surface desorption causing the steady decrease in the vertical growth rate. Linear nanowire deposition requires a steady growth rate so, unfortunately, nanowire bending is observed. Specifically, it was found that the temperature at the BIR gradually increases as

the nanowire lengthens due to a combination of thermal resistance and Joule heating, the latter produced by the spatial convolution of the electron scattering beam interaction volume with the deposit. A thermal gradient rapidly develops along the nanowire axis following beam displacement to a new exposure pixel and quickly reaches a new steady state in  $\mu\text{s}$ . The total beam exposure time per pixel is on the (ms) timescale so steady-state heating prevails during 3D FEBID.

FEBID is sustained by precursor surface diffusion from a precursor reservoir adjacent to the BIR. A steep concentration gradient develops as the nanoscale electron beam dissociates precursor in the BIR leading to monolayer growth on the scale of (ms). However, the precursor reservoir adjacent to the BIR is maintained by physisorption, also on the (ms) timescale, and the steady decrease in precursor surface residence time caused by beam heating reduces the reservoir precursor concentration over time causing the observed vertical growth rate reduction. A compensation method where the dwell time per pixel is constantly increased has been employed to maintain a constant vertical growth rate resulting in linear segments with constant thickness with elongation.

Electron beam induced heating in deposits from a variety of precursors remains to be investigated. A comprehensive examination of the heat compensation through experiments is poised to begin for deposits with electron and ion beams. The compensation method will be integrated with the FEBID CAD 3BiD program for general use.

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## **Appendices**

## Appendix A: 1D Beam Heating Model – T vs s

```
# Incoming
# -----
# {sBar} = Deposit total length [nm]
# {sBar_p} = Pillar exposure element height [nm]
# {Plot_On} = Display each T vs s plot? [0/1]

# Outgoing
# -----
# {T_max} = Maximum BIR temperature

def heatEBiD(sBar, sBar_p, Plot_On):
    import math
    import matplotlib.pyplot as plt
    import numpy as np

    # Function List
    # -----
    -

    # alpha (function #1)
    # -----
    -

    # Average, primary electron pathlength through the composite, for
    irradiation
    # at {sBar} and assuming linear primary electron path

    # Incoming
    # -----
    -

    # {zeta} = segment angle [deg]
    # {h} = segment thickness (normal to pathlength) [nm]
    # {sBar_q} = Maximum primary electron pathlength at energy (E) [nm]
    # {sBar_p} = pillar length [nm]
    # {sBar} = total deposit length [nm]
    # {d_L} = Pillar-segment transition length [nm]
    # {L_p} = Effective pillar length [nm]

    # Outgoing
    # -----
    -

    # {dz} = average, primary electron pathlength through the deposit, or
    # so-called 'absorption thickness'

    def alpha(zeta, h, sBar_q, sBar_p, sBar, L_p, d_L):
        # Pillar/segment test ['Segment' = true]
        seg = sBar >= sBar_p # [0/1]
        # Default absorption thickness ('Pillar' element thickness)
        dz = sBar_p # [nm]
```

```

    # ...segment
    if seg == True:
        # Segment exposure element length
        sBar_s = sBar - sBar_p # [nm]
        # Critical segment angle defining boundary between segment
absorption
        # thickness model based on rectangular segment cross-section
        zeta_c = math.degrees(math.atan(sBar_s / h)) # [deg]
        # Relatively 'low' segment angle
        if zeta <= zeta_c:
            # Absorption thickness
            dz = h / math.cos(math.radians(zeta)) # [nm]
        elif zeta > zeta_c:
            # Absorption thickness
            dz = sBar_s / math.sin(math.radians(zeta)) # [nm]
        # Absorption thickness ...considering pillar-to-segment transition
        dz = sBar_p + ((dz - sBar_p) / 2) * (1 + math.tanh((sBar - L_p) /
d_L))

        # Absorption thickness may not exceed the maximum, primary electron
        # pathlength through the solid
        if dz > sBar_q:
            # Maximum absorption thickness
            dz = sBar_q # [nm]

    return dz # [nm]

# compositeModel (function #2)
# -----
-
# Composite material properties computed based on the volume percent of
# each phase in the composite

# Incoming
# -----
-
# {rho_1} = density (matrix) [g/cm3]
# {Z_1} = atomic number (matrix) []
# {A_1} = atomic weight (matrix) [g/mol]
# {e_1} = energy required to generate a secondary electron (matrix) [eV]
# {rho_2} = density (nanoparticle) [g/cm3]
# {Z_2} = atomic number (nanoparticle) []
# {A_2} = atomic weight (nanoparticle) [g/mol]
# {e_2} = energy required to generate a secondary electron (nanoparticle)
[eV]
# {mat_Me} = number of matrix atoms per metal atom in composite

# Outgoing
# -----
-

```

```

    # {e_ptc} = energy required to generate a secondary electron (composite)
[eV]
    # {rho} = density (composite) [g/cm3]
    # {Z} = atomic number (composite) []
    # {AW} = atomic weight (composite) [g/mol]

    def compositeModel(rho_1, Z_1, A_1, e_1, rho_2, Z_2, A_2, e_2, mat_Me):
        # Constant (Avogadro's number)
        avogadro = 6.02214076E+23 # [atoms/mol]

        # Nanoparticle - matrix composite properties
        # -----

        # Atomic volume (matrix)
        c_aV = A_1 / (avogadro * rho_1) # [cm3]
        # Atomic volume (metal)
        pt_aV = A_2 / (avogadro * rho_2) # [cm3]
        # Molecular volume
        ptc5_aV = pt_aV + (mat_Me * c_aV) # [cm3]
        # Volume percent metal phase
        pt_V = pt_aV / ptc5_aV # [0-1]
        # Volume percent matrix phase
        c_V = 1 - pt_V # [0-1]

        # Energy required to create a secondary electron (volume percent
weighted)
        e_ptc = (c_V * e_1) + (pt_V * e_2) # [eV]
        # Composite density (volume percent weighted)
        rho = (c_V * rho_1) + (pt_V * rho_2) # [g/cm3]
        # Atomic number (volume percent weighted)
        Z = (c_V * Z_1) + (pt_V * Z_2) # []
        # Atomic weight (volume percent weighted)
        A = (c_V * A_1) + (pt_V * A_2) # [g/mol]

        return e_ptc, rho, Z, A # [eV,g/cm3,[],g/mol]

    # lossModel (function #3)
    # -----

    # Fraction of total inelastic electron energy loss that goes toward
heating
    # the deposit

    # Incoming
    # -----

    # {f_SE} = fraction of inelastic energy loss that goes toward secondary
# electron production [0-1]
    # {E_SE} = secondary electron energy [eV]
    # {e_ptc} = energy required to generate a secondary electron (composite)
[eV]

```

```

# Outgoing
# -----
-
# {f_u} = total Joule heating fraction of total inelastic electron energy
loss
# [0-1]

def lossModel(f_SE, E_SE, e_ptc):
    # Inelastic energy lost directly to the solid + energy lost after SE
    # creation as relaxation of SE ejection site to equilibrium
    f_u = (1 - f_SE) + f_SE * ((e_ptc - E_SE) / e_ptc) # [0-1]

    return f_u # [0-1]

# inelastic (function #4)
# -----
-
# Inelastic electron energy loss 'Bethe' model

# Incoming
# -----
-
# {rho} = density (composite) [g/cm3]
# {Z} = atomic number (composite) []
# {AW} = atomic weight (composite) [g/mol]
# {E} = Incident primary electron energy [keV]

# Outgoing
# -----
-
# {dE_dS} = Total inelastic electron energy loss [keV/nm]

def inelastic(rho, Z, A, E):
    # Mean ionization potential
    J = ((9.76 * Z) + (58.5 / (Z ** 0.19))) * 1E-3 # [keV]
    # Bethe model of inelastic electron energy loss
    C_1 = 78500 * rho * Z / A # [mol/cm3]
    C_2 = 1.166 / J # [keV-1]
    # Bethe model of inelastic electron energy loss
    dE_dS = ((C_1 / E) * np.log((C_2 * E) + 1)) * 1E-7 # [keV/nm]

    return dE_dS # [keV/nm]

# csAreaModel (function #5)
# -----
-
# Mathematical model describing the cross-sectional area of the segment
# exposure element. A superellipse model is applied.

# Incoming

```

```

# -----
-
# {h_x} = elliptical half-width [nm]
# {h_y} = elliptical half-thickness [nm]
# {n} = superellipse exponent [>1]

# Outgoing
# -----
-

# {A_s} = segment cross-sectional area

def csAreaModel(h_x, h_y, n):
    # Segment cross-sectional area (superellipse)
    A_s = 4 * h_x * h_y * ((math.gamma(1 + (1 / n))) ** 2) / \
        (math.gamma(1 + (2 / n))) # [nm2]

    return A_s # [nm2]

# geoFactor (function #6)
# -----
-

# A geometric factor appearing in the analytical solution for T(s)

# Incoming
# -----
-

# {s} = pathlength along the deposit [nm]
# {A_p} = cross-sectional area of the pillar [nm]
# {A_s} = cross-sectional area of the segment [nm]
# {L_p} = effective pillar length [nm]
# {d_L} = pillar-to-segment transition length [nm]

# Outgoing
# -----
-

# {A_s} = segment cross-sectional area [nm2]
def geoFactor(s, A_p, A_s, L_p, d_L):
    # Geometric factor upper integral limit
    G_F = ((d_L * (A_p - A_s) * (np.log(((A_s - A_p) * (np.sinh((s - L_p)
/ d_L))) \
                                                    + ((A_p + A_s) * (np.cosh((s -
L_p) / d_L)))))) \
        + ((A_p + A_s) * (s - L_p))) / (2 * A_p * A_s) # [1/nm]

    return G_F # [1/nm]

# Script (Main)
# -----
-

# -----
-

```

```

# User Input
# -----

# -----

# Deposit characteristics
# -----

# Segment angle
zeta = 30 # [deg]
# Pillar radius
r_p = 32.2 # [nm] 35
# Segment width (normal to pathlength through deposit)
h_x = 28.3 # [nm]
# Segment thickness (normal to pathlength through deposit)
h_y = 91.6 # [nm]
# Exponent defining the cross-sectional area of the segment
n = 2.5 # []
# Maximum primary electron pathlength at energy (E)
sBar_q = 155 # [nm]
# Pillar exposure element height
sBar_p = 400 # [nm]

# Density (matrix)
rho_1 = 1.25 # [g/cm3]
# Density (nanoparticle)
rho_2 = 21.09 # Pt atomic density [g/cm3]
# Atomic number (matrix)
Z_1 = 6 # []
# Atomic number (nanoparticle)
Z_2 = 78 # []
# Atomic weight (matrix)
A_1 = 12.0107 # [g/mol]
# Atomic weight (nanoparticle)
A_2 = 195.078 # [g/mol]
# Energy required to generate a secondary electron (matrix)
e_1 = 80 # [eV]
# Energy required to generate a secondary electron (nanoparticle)
e_2 = 30 # [eV]
# Number of matrix atoms per metal atom in composite
mat_Me = 5 # matrix:metal ratio

# Substrate oxide layer thickness
h_s = 5 # [nm]
# Substrate temperature
T_sub = 294 # [K]

# Thermal conductivity (composite)
k = 0.16 # [W/m/K]
# Thermal conductivity (native oxide surface layer)

```

```

k_s = 1.3 # [W/m/K]

# Primary electron energy
E = 30 # [keV]
# Primary electron beam current
i_b = 32 # [pA]
# Fraction of inelastic energy for SE creation
f_SE = 0.6 # [0-1]
# SE energy created in deposit (mean)
E_SE = 19 # [eV]

# Advanced Input
# -----

# Pathlength integration step
ds = 1 # [nm]
# Pathlength increment for T(s)
ds_2 = 5 # [nm]
# Primary electron elimination energy
E_o = 0.1 # [keV]

# Units Conversions
# -----

# [Joules] per [eV]
J_per_eV = 1.60218E-19 # [Joules]
# [eV] per [keV]
eV_per_keV = 1000 # [eV]
# [A] per [pA]
i_b = i_b * 1E-12 # [A]
# Thermal conductivity of deposit
k = k * 1E-9 # [W/nm K]
# Thermal conductivity of native oxide layer on substrate
k_s = k_s * 1E-9 # [W/nm K]

# Constants
# -----

# Charge per electron
q_e = 1.60217662E-19 # [C/e-]

# Scalars, Vectors, Matrices and Arrays
# -----

# Calculation of the geometry dependent function (G) used to describe
# the cross-sectional area transition from pillar to segment
# Pillar-segment transition length
d_L = r_p / math.cos(math.radians(zeta)) # [nm]
# Effective pillar length
L_p = sBar_p + d_L # [nm]

```

```

# Primary electron pathlength through solid for tip irradiation
# Inbound units --> [deg,nm,nm,nm,nm,nm,nm]
dz = alpha(zeta, h_y, sBar_q, sBar_p, sBar, L_p, d_L) # [nm]

# Composite material properties computed based on the volume percent of
# each phase in the composite
# Inbound units --> [g/cm3,[],g/mol,eV,g/cm3,[],g/mol,eV,[]]
c_M = compositeModel(rho_1, Z_1, A_1, e_1, rho_2, Z_2, A_2, e_2, mat_Me)

# Density (composite)
rho = c_M[1] # [g/cm3]
# Atomic number (composite)
Z = c_M[2] # []
# Atomic weight (composite)
A = c_M[3] # [g/mol]
# Energy required to generate a secondary electron (composite)
e_ptc = c_M[0] # [eV]

# Fraction of total inelastic electron energy loss that goes toward
heating
# the deposit
# Inbound units --> [0-1,eV,eV]
f_u = lossModel(f_SE, E_SE, e_ptc)

# Number of integration steps
N = int(math.floor(dz / ds))
# Inelastic energy loss accumulation 'Bethe' model
q = 0 # [keV/nm]
# Integration step counter
n = int(0)

# ...integration steps finite AND primary electron exists
while n <= N and E > E_o:
    # Advance integration step
    n = n + 1 # [1,2,3,...]

    # Inelastic electron energy loss 'Bethe' model
    # Inbound units --> [g/cm3,[],g/mol,keV]
    dE_ds = inelastic(rho, Z, A, E) # [keV/nm]

    # Integrated electron energy loss
    q = q + dE_ds # [keV/nm]
    # Primary electron energy decay
    E = E - dE_ds # [keV/nm]

# Deposit Joule heating rate
q = (q * eV_per_keV * J_per_eV) * ds * f_u * i_b / q_e # [J/s]

# Pillar cross-sectional area (circular)
A_p = math.pi * r_p ** 2 # [nm2]

```

```

# Half minor segment axis
h_x = h_x / 2 # [nm]
# Half major segment axis
h_y = h_y / 2 # [nm]

# Segment cross-sectional area (superellipse)
# Inbound units --> [nm,nm,[>1]]
A_s = csAreaModel(h_x, h_y, n) # [nm2]

# Analytical solution to Fourier's Law
# -----

# Calculation of the geometry dependent function (G) used to describe
# the cross-sectional area transition from pillar to segment

# Total pathlength along calibration structure
s = np.arange(ds_2, sBar + ds_2, ds_2) # [nm]

# A geometric factor appearing in the analytical solution for T(s). Upper
# integration limit
# Inbound units --> [nm,nm2,nm2,nm,nm]
G_F = geoFactor(s, A_p, A_s, L_p, d_L) # [1/nm]
# Geometric factor lower integration limit
G_i = geoFactor(0, A_p, A_s, L_p, d_L) # [1/nm]
# Area variation geometric factor (G)
G_S = G_F - G_i # [1/nm]

# Final temperature at beam impact region, or BIR
T_s = T_sub + (q / k_s) * (h_s / s) * G_S + (q / k) * G_S # [K]

# Export data as text file --> T_vs_s.txt
# -----

# Open text file ...with variable file name
txt = "T_vs_s_{Dep:.0f}_nm.txt"
# Insert variable into the file name
fileName = txt.format(Dep=sBar)
# Open file for writing
file = open(fileName, 'w')
# ...data points
for m in range(0, len(s)):
    # write line [m]
    file.write("{0}\t{1:.3f}\n".format(s[m], T_s[m]))
file.close()

# Plot Output
# -----
if Plot_On == 1:
    plt.plot(s, T_s, 'k--')
    plt.ylabel('T (K)')
    plt.xlabel('s (nm)')

```

```
plt.show()

# print('Maximum, BIR temperature (K)')
# print(T_s[len(T_s)-1])

# Maximum temperature ...at BIR
return T_s[len(T_s) - 1]
```

## Appendix B: 1D Beam Heating Model – $T_{\max}$ vs $S$

```
import beamHeating as bh
import numpy as np
import matplotlib.pyplot as plt

# Script (Main)
# -----
# -----

# User Input
# -----
# -----
# Deposit length (range)
# -----
# Deposit length (minimum)
sBar_Min = 10 # [nm]
# Deposit length (maximum)
sBar_Max = 800 # [nm]
# Deposit length (increment)
dS = 5 # [nm]

# Pillar exposure element height
sBar_p = 400 # [nm]

# Plot T(s) for each (S)?
Plot_On = 0 # [0/1]

# Scalars, Vectors, Matrices and Arrays
# -----
# Segment angle (vector)
sBar = np.arange(sBar_Min, sBar_Max+dS, dS) # [deg]
# Maximum temperature (vector)
T_max = np.zeros(len(sBar), dtype='d') # [K]

# ...total deposit length
for n in range(0, len(sBar)):
    # Maximum temperature {n}
    # Inbound units --> [nm, nm, [0/1]]
    T_max[n] = bh.heatEBiD(sBar[n], sBar_p, Plot_On) # [K]

# Export data as text file --> Tmax_vs_S.txt
# -----
# File name
fileName = "T_vs_S.txt"
# Open file for writing
file = open(fileName, 'w')
# ...data points
```

```
for n in range(0,len(sBar)):
    # write line [m]
    file.write("{0}\t{1:.3f}\n".format(sBar[n],T_max[n]))
file.close()

# Plot Output
# -----
plt.plot(sBar, T_max, 'k--')
plt.ylabel('T_max (K)')
plt.xlabel('S (nm)')
plt.show()
```

## **Vita**

Eva Mumbua Mutunga was born in Nairobi, Kenya to Joel and Rhoda Ngundo. She is the fourth of five children, Lucy, Nancy, Catherine, and Winnie. She earned an Associate of Science in Engineering from Anne Arundel Community College and a Bachelor of Science in Mechanical Engineering from The University of the District of Columbia. Eva is a graduate research assistant in the Bredesen Center for Interdisciplinary Research and Graduate Education, working on a PhD in Energy Science and Engineering.