

Simulation Guided 3D Nanomanufacturing via Focused Electron Beam Induced Deposition

Jason D. Fowlkes^{a,b}, Robert Winkler^c, Brett B. Lewis^b, Michael G. Stanford^b Harald Plank^{c,d} and Philip D. Rack^{a,b}

^a Nanofabrication Research Laboratory, Center for Nanophase Materials Sciences, Oak Ridge National Laboratory, Oak Ridge, Tennessee 37831, United States

^b Materials Science and Engineering Department, The University of Tennessee, Knoxville, Tennessee 37996, United States

^c Graz Centre for Electron Microscopy, Steyrergasse 17, 8010 Graz, Austria.

^d Institute for Electron Microscopy and Nanoanalysis, Graz University of Technology, Steyrergasse 17, 8010 Graz, Austria

This manuscript has been authored by UT-Battelle, LLC under Contract No. DE-AC05-00OR22725 with the U.S. Department of Energy. The United States Government retains and the publisher, by accepting the article for publication, acknowledges that the United States Government retains a non-exclusive, paid-up, irrevocable, world-wide license to publish or reproduce the published form of this manuscript, or allow others to do so, for United States Government purposes. The Department of Energy will provide public access to these results of federally sponsored research in accordance with the DOE Public Access Plan (<http://energy.gov/downloads/doe-public-access-plan>).

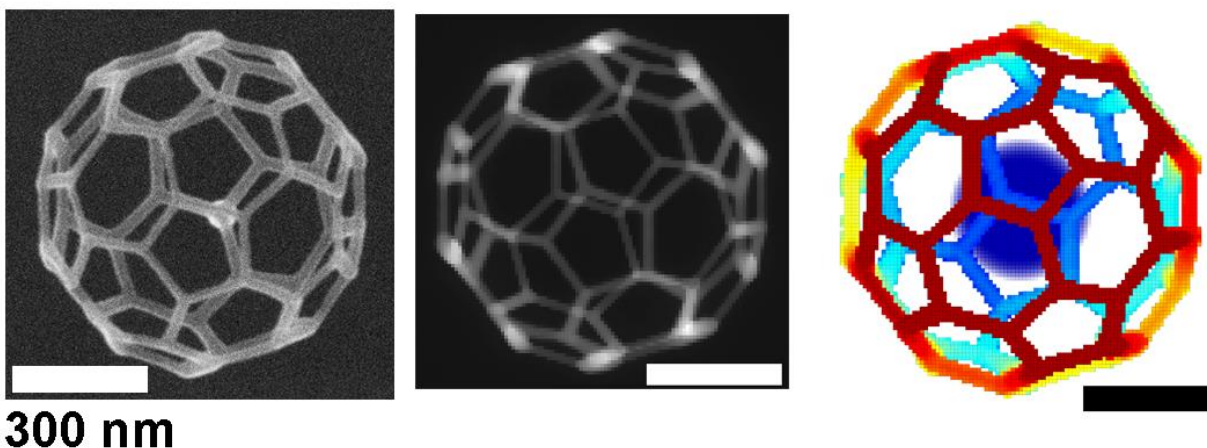


Table of Contents graphic

Abstract

Focused electron beam induced deposition (FEBID) is one of the few techniques which enables direct-write synthesis of free-standing 3D nanostructures. While the fabrication of simple architectures such as vertical or curving nanowires have been achieved by simple trial and error, processing complex 3D structures are not tractable with this approach. In part, this is due to the dynamic interplay between electron–solid interactions and the transient spatial distribution

of absorbed precursor molecules on the solid surface. Here, we demonstrate the ability to controllably deposit 3D lattice structures at the micro/nanoscale which have received recent interest owing to superior mechanical and optical properties. A hybrid Monte Carlo-continuum simulation is briefly overviewed and subsequently FEBID experiments and simulations are directly compared. Finally, a 3D computer aided design (CAD) program is introduced, which generates the beam parameters necessary for FEBID by both simulation and experiment. Using this approach, we demonstrate the fabrication of various 3D lattice structures using Pt, Au and W based-precursors.

Keywords: 3D nanoprinting, direct write, focused electron beam induced deposition, nanofabrication

Resist-free, direct write additive manufacturing techniques ideally allow for the fabrication of functional micro- and nanostructures on practically any given surface including where classical resist-based techniques cannot be used. In particular, focused electron beam induced deposition (FEBID) is attracting increasing attention owing to sub-10 nm^{1, 2} resolution while being one of the few techniques which allows truly three-dimensional (3D) fabrication. FEBID uses a nanoscale focused electron beam to dissociate adsorbed precursor molecules. A condensed deposit forms as a result of dissociation at the beam-precursor intersection. Appropriate sequential beam scanning in the substrate plane (x-y) can generate out-of-plane deposition (z) forming a 3D deposit. Thus, FEBID has the potential to be a versatile 3D additive nanomanufacturing technique.

Nanohelix metamaterial arrays have recently been deposited over tens of microns by FEBID representing the current state-of-the-art in nanoscale 3D direct-write³. Also, 3D FEBID has recently been demonstrated using a nanoelectrospray liquid precursor injection method⁴. In the previous two decades arches^{5, 6}, angled segments⁷ and helices^{8, 9}, optically active pillar arrays¹⁰, square frame antennas¹¹ and electron optics¹² have been demonstrated. Matsui demonstrated solid object, layer-by-layer deposition of complex 3D replicas using the Ga⁺ ion beam as well as helices¹³ and angled segments¹⁴. Moving forward, more and more complex 3D objects relevant to nanoscale prototyping will be required. Thus, design by simulation is required to both predict the ideal scanning pattern and tackle complex 3D designs in order to avoid time consuming trial and error approaches typically used.

In the past, we have reported a Monte Carlo simulation^{15, 16}, coupled with an atomic level handling of the precursor-solid interaction for the purpose of understanding FEBID related phenomena at the nanoscale, but this method can be intractable for simulating relatively large scale features. For example, each precursor molecule was handled as a discrete particle that executed a random-walk motion to emulate the diffusion of the virtual molecule on the deposit surface¹⁷, a computationally expensive process. Conversely, we¹⁸ and others¹⁹⁻²¹ have also created pseudo 2D continuum simulations applicable for larger length scales for the purpose of computationally extracting material parameters as well as for understanding basic scanning induced growth regimes^{22, 23}. The 2D simulation²⁴ however, is a more suitable approach for depositing simple structures within the limit of small and finite surface curvature, and is incapable of treating truly 3D structures. Recent developments in continuum modeling²⁰ have

made it possible to elucidate critical precursor–solid parameters²⁵ using fully 3D simulations. Here, we report a full 3D simulation which bridges the spatial length scale between approximately 10 nm and 1 μm and is capable of replicating complex lattices/meshes deposited by experimental FEBID.

We overview the elements incorporated into a hybrid Monte Carlo–continuum simulation²⁶ while referencing previously reported details. After the brief simulation overview, we focus on the comparison between experiments and simulations. The FEBID simulation is calibrated based on careful experiments and implementing materials parameters available in the literature. A major aspect of this work is the successful convergence of experiments and simulations. Following this convergence, a CAD program was created for the purpose of designing complex 3D geometries as input for both FEBID simulations and experiments. The CAD program output is a data set including beam spatial coordinates and beam dwell times necessary to generate the prescribed 3D object. Robustness was tested by executing 3D FEBID on two different dual beam machines. 3D objects (ring, frame, cube and icosahedron geometries, all in mesh form) predicted by simulation were replicated across both microscopes with a nanoscale level of resolution.

Simulation Description

The results of a FEBID simulation are shown in figure 1a. Details related to the 3D rendition are provided in S1. First, a vertical nanopillar was deposited using a stationary beam dwell of 2.4 s. This nanopillar served as a support for the subsequent deposition of a suspended segment. The segment was grown by translating the virtual electron beam (FWHM = 4nm), parallel to the substrate plane, using a digital step length of 0.2 nm and an exposure time of 2.4 ms. The geometry presented in figure 1a serves as a model structure to describe the simulation details in the following simulation overview.

Overview

The hybrid Monte Carlo–continuum simulation consists of two distinct parts: a Monte Carlo simulation which calculates the electron–solid interaction (figure 1b) and a FEBID simulation of precursor surface adsorption, transport and deposition. The FEBID simulation consists of two main subroutines.

In the first subroutine, electron trajectories, derived in the Monte Carlo simulation, are adapted to the shape of the evolving 3D deposit (figure 1c). Electron trajectory adaption is the first step toward generating an emitted secondary electron distribution and an effective secondary electron current density over the surface of the 3D deposit. This subroutine is executed each time the electron beam is displaced to the next position on the 3D deposit surface, *i.e.*, at the beginning of each unique dwell time (τ_d).

In the second subroutine, the coupled rate equations describing precursor adsorption, desorption, surface diffusion, dissociation and deposition are solved. In particular, the rate equation describing deposition includes the emitted secondary electron current density profile derived from the adapted Monte Carlo subroutine. The second subroutine is executed

repeatedly during each dwell time, with a time step ($\Delta t \ll \tau_D$), in order to simulate time-dependent changes in precursor coverage and electron beam induced dissociation dynamically during the continuous electron irradiation.

Monte Carlo simulation

The Monte Carlo algorithm, which is executed first, generates a series of unique electron trajectories in an infinite 3D domain which is larger than the beam impact region (BIR) so as to fully encapsulate the electron trajectory (figure 1b). The domain has the material properties (density, atomic weight and density) characteristic of the deposit material. Each electron starts at an embedded virtual beam position of (x_i, y_i, z_i) , parallel to the $-z$ direction and with an initial energy of E_0 . Elastic (Rutherford cross-section) and inelastic (continuous slowing down approximation) scattering processes²⁷ occur as the electron propagates through the solid until the electron reaches a cutoff energy of 100eV where the Monte Carlo routine stops (see S2 for the justification). Each electron scattering event is characterized by (1) the (x, y, z) coordinates and (2) the inelastic electron energy loss (and subsequently the primary electron energy). This information is saved to a file for use in the FEBID simulation.

FEBID simulation

Subroutine #1: electron trajectory adaption

Electron trajectories originally calculated in the extended solid are adapted to construct the beam interaction volume and its convolution with the 3D deposit. Electron trajectory adaption to the deposit includes accounting for the real Gaussian beam shape, electron transport through vacuum upon escape from the deposit surface, in which no scattering occurs, and primary electron reentry into the deposit as described in detail in S3. The 3D deposit is contained within a domain of cubic voxels. Each voxel has a unique material identifier; 'B' indicating bulk/deposit, 'V' vacuum/vapor phase and 'S' a surface voxel. Each electron trajectory is adapted to the 3D deposit by first shifting the initial coordinate (x_i, y_i, z_i) of the sampled trajectory to the beam-deposit surface impact point (figure 1c). An additional displacement is executed to reconstruct the Gaussian shape of the focused electron probe (figure 1c). The current model does not include the effect of beam de-focus in the z -coordinate, which for the small structures demonstrated, is appropriate. Subsequently, each additional (x, y, z) coordinate defining the scattering path is referenced to the voxel that it intersects. A statistically significant (S4) number of primary electron trajectories are used and scaled to generate the required total dose per dwell time.

Inelastic electron energy loss (dE/ds) (see Methods) occurs if an electron passes through a 'B' voxel. A fraction of the energy loss (f) leads to secondary electron generation according to;

$$n_{SE} = \frac{f}{\varepsilon} \frac{dE}{ds} \Delta s \quad [1]$$

where (n_{SE}) is the number of secondary electrons created, (ε) is the energy required to create a secondary electron and (Δs) is the path length of the electron trajectory that intersects the

specific 'B' voxel. Data for (f) is unavailable for the deposited material composition (PtC₅) so (f) was arbitrarily set to equal to 1 and $\varepsilon=73$ eV was calculated from atomic values available for Pt ($\varepsilon=30$ eV) and C ($\varepsilon=80$ eV), using atomic averaging from Lin *et al.*²⁸. Conveniently, these values recovered the experimentally measured SE yield of 0.1 which provided an additional calibration between simulations and experiments. Liberated secondary electrons are emitted in an isotropic geometry from an origin located along the primary electron scattering trajectory. Random spherical point picking is used to generate each SE electron trajectory where the radius of the sphere is equal to the secondary electron mean free path. The number of secondary electrons that traverse each surface voxel "S" are accumulated, then stored, as input for integration with the continuum rate equations. The result is a three-dimensional secondary electron surface emission profile, constructed using;

$$i_{SE}(x, y, z) = \frac{\sum n_{SE}}{\left(\frac{n_{PE}q}{i_b}\right)(\Delta z^2)} \quad [2]$$

where $(n_{PE}q/i_b)$ is the time for n_{PE} electrons to impact the deposit for the primary electron beam current setting of i_b , q is the charge per electron and Δz^2 is the surface area per surface voxel (S5) face yielding the electron flux term $i_{SE}(x,y,z)$.

Finally, in the event that an electron passes through a vacuum voxel 'V', the electron trajectory is extended along its current trajectory until the electron either reenters the solid or exits the simulation domain. In the former case, the remaining coordinates defining the total scattering path are also shifted by the translation in the vacuum and the electron trajectory continues scattering in the solid (figure 1c). In the latter case, the current trajectory is terminated.

The various length scales of the simulation are shown in figure 1d. A single voxel ($\Delta z = 8$ nm edge length) in the simulation domain is shown as (1) in the inset, the inset boundaries define a typical continuum simulation domain size (720nm) inset (2) while the main figure 1d window shows a cross-section through the buried beam impact point in the Monte-Carlo simulation for 30keV point electron source.

Subroutine #2: rate equation solver

The time-dependent precursor surface concentration at each surface voxel in the simulation is described by;

$$\frac{\partial C(x, y, z)}{\partial t} = D\nabla^2 C(x, y, z) + \delta\Phi(x, y, z) \left[1 - \frac{C(x, y, z)}{s_p}\right] - \frac{C(x, y, z)}{\tau} - \sigma C(x, y, z) i_{SE}(x, y, z) \quad [3]$$

where the terms appearing on the right-hand side, moving from left-to-right, treat precursor surface diffusion, adsorption, desorption and the electron beam induced dissociation, respectively. The precursor surface impingement flux $\Phi(x,y,z)$ is treated as space-dependent (figure 1e) because past experiments have revealed that the precursor flux has both diffuse and directed contributions²⁴, an effect observed previously by Bret *et al.*²⁹ and Friedli *et al.*³⁰ The directed component of the precursor flux is space-dependent and depends critically on the

orientation of the surface normal vector with respect to the so-called gas flux vector (GFV) of the precursor beam emerging from the gas injection system. The gas flux vector is the propagation vector of the directed portion of the precursor “beam”. S6 provides details on the how the directed gas flux is calculated. The diffuse gas flux is assumed to be constant over the entire simulation domain containing the deposit. Importantly the surface flux calculation requires knowledge of the surface normal and the method used to approximate the surface normal is also provided in S6.

Simulation Parameters

PtC₅ deposits were grown using the MeCpPt^{IV}Me₃ precursor using an electron beam acceleration voltage (E_0) of 30 keV, a beam current (i_b) of 21 pA and a local, total precursor pressure (P_T) of 30 mTorr. A stationary electron beam dwell was used to determine the electron yields from the surface; the secondary electron yield per incident primary electron (δ_{SE}) was 0.1 for a flat, semi-infinite PtC₅ substrate. The equilibrium precursor surface coverage (θ_0) for the flat PtC₅ surface for our gas injection system was calculated to be 0.73 when the precursor nozzle was oriented at 38° with respect to the substrate normal vector and the precursor capillary tube. Parameters necessary for this calculation were (1) the precursor sticking probability (unknown, assumed $\delta=1$), (2) the surface diffusion coefficient 0.4 $\mu\text{m}^2/\text{s}$ of MeCpPt^{IV}Me₃³¹ and (3) the mean surface residence time (τ) of 100 μs for the MeCpPt^{IV}Me₃ molecule adsorbed on PtC₅¹⁶. Regarding the parameter (τ), an experimentally derived value of ~29 μs is reported in the literature³² yet we have found that by increasing the parameter to 100 μs a better fit to our experiments is achieved¹⁶. Additional information regarding the experiments is provided in the Methods section.

The model applied in the simulation assumes that only secondary electrons contribute to electron impact dissociation³³. Forward scattered electrons (FSE) and backscattered electrons (BSE) influence precursor dissociation indirectly, through the SEs that they generate as the exit/reenter the deposit or substrate. The SE driven precursor dissociation is well-known to be the highest probability pathway for dissociation³⁴. A mean dissociation cross-section ($\sigma=0.013 \text{ nm}^2$) was determined by integrating the energy dependent cross-section, reported in³⁵, over the SE emission range 0–50 eV weighted to the number of SEs emitted per unit energy²⁴. The Methods also contains a complete table of parameters used in the simulation.

A floating parameter for this simulation was introduced to fit the remaining difference between experiments and simulations. This parameter is defined as the variable χ , and the best fit value was $\chi=2.1$ (see S7 for effect of χ and τ_d). This parameter was multiplied by σ in order to increase the FEBID growth rate for the simulations. The contribution of primary, backscattered and forward scattered electrons to FEBID are ignored as well as low energy electron attachment reactions which could account for some fraction of χ .

Results and Discussion

Simulation Accuracy & Information Recovery

The predecessor to this simulation was a 2D hybrid Monte Carlo & continuum simulation reported in²⁴. The simulation includes (1) the implications of the precursor beam or GFV and (2) beam scanning but excludes (1) a treatment of precursor diffusion in 3D and assumes (2) growth exclusively in the vertical dimension, normal to the original substrate surface. On the one hand, the 2D simulation predicted well the effects of beam scanning strategies on nanoscale pseudo-2D deposit geometries but the approach is limited to evolving deposits with negligible surface curvature. As such, the simulation is incapable of predicting the evolution of complex 3D features. A series of test experiments are now presented, which were contrived for the purpose of reproducing pseudo 2D simulated results reported previously and to help validate the 3D simulation.

Simulations of Pseudo-2D FEBID

FEBID is used frequently to deposit thin square/rectangular prisms which serve as electrical contacts, defect repair films, etc. The thin square prism is achieved by a simple raster scanning approach even when a directed precursor beam is used²⁴. However, unwanted surface artifacts evolve for more complex scanning strategies. An outward spiral scanning tactic is shown in figure 2(a). This pattern leads to the deposition of peculiar surface features in part because the beam trajectory switches abruptly between trajectories toward, away from and perpendicular to the GFV²⁴. The GFV orientation with respect to the shot pattern, and projected on the (x-y) plane, is provided figure 2(a). The GFV is oriented at 38° with respect to the substrate surface normal for the experiments and simulations reported here. The colored 2D AFM height image map in figure 2(a) shows the experimental results of such a scanning strategy.

A nanoscale surface morphology evolves with four distinct terraces for the spiral-out patterning. An acceleration voltage of 5 keV and a beam current of 400 pA were used to deposit the pattern²⁴. The characteristic size of the beam was FWHM=27.1 nm with a pixel point pitch of 13 nm and a 1 ms beam dwell per pixel point. A purely directional beam producing a local precursor pressure of 15 mTorr at the growth surface reproduced experimental results using the pseudo-2D simulation²⁴. The 3D simulation reported here reproduced the pseudo-2D simulation results reported previously with a slight adjustment in some parameters S8.

The terraced surface morphology of the thin square prism was recovered using the 3D simulation (figure 2(b)). The 3x3 vertical voxel slice illustrates the fractional deposit occupancy near the surface of the deposit. One goal of the current 3D simulation is to make multi-length scale simulations more tractable. Numerical stability is maintained during the finite difference part of the sub-routine if $(\Delta t \cdot D / \Delta z^2) < 0.125$ is satisfied. It was determined that Δz could be increased up to a length of 8 nm without sacrificing the desired nanoscale resolution. Moreover, the voxel size of 8 nm was found to yield an execution speed comparable with the 2D simulation while slightly sacrificing lateral resolution as evident in the 3D plot in figure 2b. Conveniently, accounting of partial voxel filling in the simulation and the voxel surface normal routine (S6) effectively reveals growth features at sub-voxel resolution. In the case of the square prism, the deposit growth front proceeds predominantly in the vertical direction (z) over all (x,y) space. Thus, the summation of voxel occupancy in the z-dimension estimates well sub-voxel detail as shown in figure 2(c). The 3x1 voxel array is the summation of voxel occupancy in the 3x3 slice

in figure 2(b). The simulation reveals important details such as the trenches between the terraces which were also observed in experiments but not revealed by the previous pseudo-2D simulation. The maximum height of the simulated prism (57 nm) matched experiments (62 nm) as well as the ratio of ledge heights (min/max simulation = 0.65, experiment 0.68) S9. Figure 2(d) shows an AFM image of the complementary thin film prism deposited experimentally.

Advanced 3D Simulations

Experiments revealed that the most resolved 3D structures are produced at the highest possible primary energy (30 keV), for conventional field-emission SEMs, and a relatively low current (21 pA) as reported previously^{36, 37}. Figure 3 shows an SEM image of an array of angled segments, supported by vertical pillars, deposited with a variable dwell time (3–50 ms) for $\Lambda = 1$ nm. The ‘segment’ geometry is a critical basic element required to create any 3D object with a mesh or lattice structure^{13, 14, 38}. The insets representatively show complementary segments deposited from the Au and W containing organometallic precursors dimethylgold acetylacetonate³⁹ and tungsten hexacarbonyl, respectively, demonstrating the applicability of the 3D growth conditions to multiple precursor molecules. As lateral beam size scales inversely with PE energy and in proportion to the PE current, the experimental conditions used favored a small probe to achieve high resolution. However, the SE yield is relatively low at 30 keV making dissociation, and subsequent deposition less efficient. Ancillary deposition is therefore reduced outside the BIR.

Control of the segment angle of the growing deposit (ζ , figure 4(a)) is critical for the 3D direct-write process. Specifically, the capability to grow segments spanning from horizontal ($\zeta=0^\circ$) to vertical ($\zeta=90^\circ$) is necessary to construct all possible segment orientations for 3D objects. The segment geometry was explored here to (1) quantify the experimentally assessable direct-write angle range and to (2) test the accuracy of the simulation. The segment morphology is deposited by a two-step direct write sequence. An initial, stationary beam produces a vertical pillar morphology where the height is controlled by the total dwell time with a nearly linear dependence which suggests a steady state FEBID condition. Next, the beam is laterally displaced at constant velocity with a fixed pixel point pitch to produce the segment component. The scan speed controls the segment angle as has been observed previously⁸. The vertical pillar served as a reproducible platform for segment growth as standard substrate proximity effects are minimized for the suspended segments, particularly when using the highest primary beam energy. The stage current signal collected during EBID is sensitive to patterning changes such as the pillar to segment transition⁴⁰. S10 provides a complementary EBID simulation for the previously reported “tip on suspended rod”⁴⁰ geometry demonstrating the successful emulation of the stage current signal.

A simulated segment is shown in figure 4(a) in cross-section through the length of the segment. A top-down view of the segment is provided in the inset shown at the top. The segment width ($w=24$ nm), nanopillar diameter ($d=56$ nm), segment angle ($\zeta=42^\circ$) and thickness ($t=80$ nm) all agreed well with experimental results of segment width (26 nm), nanopillar diameter ($d=53$ nm), segment angle ($\zeta=47^\circ$) and thickness ($t=53$ nm). The experimental values were determined

from an image measurement where the image pixel size was 2.4nm. The pixel point pitch during the segment growth was 1 nm with a constant pixel dwell time of 11 ms.

Simulations also predicted the effect of beam dwell time on the segment angle figure 4(b). Lastly, experiments revealed that the angle of the GFV with respect to beam displacement vector (α), where GFV_{xy} indicates the GFV projected onto the substrate plane, had a negligible effect on the segment angle as confirmed by simulations shown in the image collage provided in figure 4(c). For reference, α is arbitrarily defined as 0° when the beam displacement vector was anti-parallel with the GFV_{xy} and 180° when parallel with the GFV_{xy} ²⁴. A previous study²⁹ has demonstrated a strong dependence on the GFV and beam scanning direction during 3D EBID. In S11, complementary 3D EBID simulations are presented that support the authors' claim that surface coverage variations dictate the final morphology for complex and highly oriented 3D surfaces."

The results presented in figure 4(b) served as a turning point for the evolution of the simulation. Previously, physical experiments were used to calibrate the 3D simulation, however, once the simulation was verified/calibrated using the results presented in figure 4(b), CAD files were generated for the desired 3D structure and exported to the simulator which tested the growth conditions which were finally verified experimentally.

Direct-Write, Computer Aided Design (CAD)

3D objects for direct-write design were first defined by vectors spanning object edges. The models are defined as 3D mesh structures with linear segments connecting object vertices. The CAD program determines each segment angle and linearly interpolates the requisite segment angle for the simulated data points in figure 4(b) to generate a stream file of x, y and τ_d coordinates for each pixel. 3D object construction requires segment connectivity to form meshes/frame elements. FEBID experiments were conducted to test the robustness and predictability of simulated designs for assembling connecting segments. A vertical and tilted frame was simulated at 30 keV, 21 pA where the lower edge of the square (segment 2 in figure 4(d)) was raised at 30° with respect to the underlying substrate. The simulated result is shown in a virtual SEM image (figure 4(e)) where the substrate has been tilted at an angle of 52° . The image has been stretched in figure 4(e) along the vertical coordinate by a factor of $1/\sin(52^\circ)$ in order to emulate the real image acquisition conditions for the complementary experiment shown in figure 4(f).

The distribution of beam shots required to deposit the square frame was divided into 4 phases. This distribution is described below while a movie of the shot distribution is provided in S12. In general, to construct multiple edge geometries two approaches are possible: 1) serial growth of entire segments or parallel growth of multiple segments. For the square geometry in figure 4(d-f) for instance one can grow segments 1 and 2 in parallel or in series followed by a series or parallel growth of segments 3 and 4. A subtle advantage is realized by doing parallel edge growth associated with: 1) the slight accumulation of precursor that occurs at each growth front when the other edge(s) are being exposed and 2) the symmetric proximal deposition that each

segment realizes relative to asymmetric proximal deposition when the exposure is executed in series. Initially, in phase 1, the *beam alternated*, per shot, between the growth of segments 1 and 2. It is important to note that segments 2 and 3 required a per-shot dwell time of 1.98 ms while segments 1 and 4 required a dwell time of 3.73 ms due to the different segment angles. The pixel point pitch was constant at 0.2 nm for all phases of exposure. As a result, during the 1st phase, segment 1 completes before segment 2. A 2nd phase then ensues where the growth of segment 2 is completed. Upon completion, segments 3 and 4 are then exposed in the same alternating fashion. Segment 4 finishes first leading to the 4th and last phase of growth where segment 3 grows to the point of frame closure. Simulation results closely replicated the experiment as highlighted in figures 4e–f. Thus, the methodology was tested further by attempting the deposition of a 3D object (figure 5a) which required the assembly of multiple frames and the final convergence to a single vertical point for high fidelity reproduction.

A 3D cube CAD file was generated, grown by experiment (figure 5a) and simulated (figures 5b–c) successfully, on the first attempt. The cube was oriented in the design phase such that all segment angles were equal. A short pedestal was initially deposited using a static dwell of 0.75 s in order to provide a take-off point for the cube edge growth. Multiple phases of parallel growth ensued which are evident in the movie provided in S12. This particular geometry requires a high density of pixel dwells (10,000) packed in a relatively small area (cube edge = 250 nm) leading to proximal deposition, or staining, on the underlying substrate. Strategies to minimize this proximity effect will be described in our near future work.

Two candidates may be responsible for deposition on the supporting substrate: 1) electrons that that ‘miss’ the leading edge of the segment and strike the underlying substrate and 2) primary electrons which transmit through the deposit and re-enter the substrate. The relative contributions can be distinguished using the simulation by correlating the scattering step number with each deposition event. The consequent secondary electrons liberated during the first scattering step of the primary electron impact are denoted as SE^A and secondary electrons generated by a scattering step > 1 are denoted as SE^B .

The fraction of deposition stimulated by SE^A (first scattering step) *versus* SE^B (scattering step > 1) was tracked for each deposit voxel. Figure 5d shows a slice through a segment grown using a dwell time of 1.6 ms and $\Lambda = 0.2$ nm where the colormap reveals the normalized fraction of deposition generated by SE^A s. The data is revealing – very little contribution arises from SE^A –induced deposition at the substrate surface. Conversely, figure 5e shows that the substrate nanowire is deposited mainly by SE^B s originating from the transmitted beam. Finally, figure 5f shows the same information in a slightly different fashion which provides insight into both modes of growth on a single figure. The 3D ‘B’ voxel–based image has been sliced down the middle to reveal the history. Red portions of the colormap are driven mostly by SE^A induced deposition while blue areas are induced by SE^B s. Also demonstrated by figures 5d–f is the relative contribution of the segment growth; the figures illustrate that the segment thickness is dominated by growth induced by the exiting beam where the growth front is in the downward direction.

A 3D truncated icosahedron mesh was deposited (figure 5g) and served as a model structure to test a more complex geometry. This geometry required 10 vertical levels of exposure forming 20 hexagons and 12 pentagons in the final mesh. Correct segment intersection at the last vertices deposited, during the last exposure level (figures 5h–i), served as a qualitative test of segment angle precision.

Conclusions

Focused electron beam induced deposition (FEBID) is capable of the direct-write of complex free-standing 3D nanostructures. Understanding the dynamic interplay of the scanning electron beam and the adsorbed precursor molecules is critical to accelerating the state of the art of FEBID as a 3D nanoprinting tool. To this end we have developed a fully 3D hybrid Monte Carlo/continuum simulation to model the growth of 3D objects *via* FEBID. Excellent agreement between experiments and simulations were realized. A CAD program which generates complex 3D structures and translates the necessary x-y coordinates and electron beam dwell times was also developed. The tractable simulation speed made it possible to test and optimize the pattern sequences to better guide our experimental capabilities for the growth of complex 3D deposits. For the case of the 3D truncated icosahedron demonstrated here, most of the critical electron–solid, precursor–solid and electron–precursor interactions critical to growth take place on the surface of deposit itself, with very little influence from the supporting substrate.

The most significant assumptions made in the simulation are as follows. The energy dependence of the total electron impact dissociation cross-section of the precursor $\sigma(E)$ is neglected in favor of a single value σ_m estimated using the mean energy of the secondary electron energy distribution²⁴. Further, the effect of secondary electron refraction at the deposit interface is ignored when SEs intersect the deposit/vacuum interface. These features were included in previous, atom level simulations¹⁶ and are necessary to accurately predict sub-10 nm surface features. Also, the directed component of the precursor beam is a highly idealized model because zero beam divergence is assumed. This simplification could lead to poor EBID emulation for the case of complex geometries which exhibit complex shadowing patterns during growth. Nonetheless, these features can be adapted into the current simulation yet were intentionally omitted in favor of simulation speed. The agreement between experiments and simulations at the mesoscopic scale validate their exclusion in the results presented here. In addition, supplements S10-11 provide complementary simulations of mesoscale artifacts reported previously^{29, 40, 41}. In the future, translation of the simulation algorithm onto a high performance computing platform will make it possible to include these features without the sacrifice of simulation process time.”

Methods/experimental

Monte Carlo simulation

The electron–solid interactions were emulated using a Monte Carlo electron scattering simulation reported previously²⁶ where a single scattering methodology was used. Elastic scattering was treated using the screened Rutherford cross-section²⁷. The inelastic energy loss was treated using the continuous energy loss approximation implementing the Joy and Luo modified Bethe expression²⁷;

$$\frac{dE}{dS} = -7.85 \times 10^4 \frac{Z}{AW \cdot E} \ln \left(\frac{1.166(E + 0.85J)}{J} \right) \quad [4]$$

where Z is the atomic number, AW is the atomic weight, E is the electron energy and J is the mean ionization potential²⁷.

Continuum Simulation

An explicit forward time marching, centered space (FTCS) difference method was used to solve the 3D parabolic diffusion equation for the case of MeCpPt^{IV}Me₃ diffusion on the PtC₅ surface. In order to emulate surface diffusion in all three Cartesian dimensions required using both 1st, and 2nd, nearest neighbour surface voxels in the centered difference approximation⁴². The improved Euler method (Huen's method) was used to approximate the ordinary differential equation describing the time-dependent surface coverage (adsorption and desorption) of MeCpPt^{IV}Me₃. Due to the coupling between diffusion and adsorption/desorption (*via equation 3*), these numerical methods had to be executed concurrently on the same time step. Numerical stability required that the time step be determined by the finite differencing method, which was $\Delta t \approx 10 \mu s$. As an example of simulation timing, equation 3 was solved consecutively, 1289 times per 11 ms beam dwell, while the Monte Carlo sampling, described previously, was recalculated at the beginning of each beam dwell, or every 11 ms.

Experimental

Two different dual beam microscopes were used for FEBID experiments: a Nova 200 and a Nova 600 (FEI Company, The Netherlands) in Austria and the US, respectively. While MeCpPt^{IV}Me₃ precursor were used on both machines, Me₂Au(acac) precursor were only used on the Nova 200 and W(CO)₆ only on the Nova 600. All experiments were performed on always new Si substrates with a 5 nm SiO₂ top-layer⁴³ which were prepared in a laminar flow box (Austria) and clean room conditions (US) and immediately transferred to the microscopes. No special substrate cleaning procedures were used. Prior to any deposition experiment, the precursor reservoirs were pre-heated to 45°C (Pt), 30°C (Au) and 55°C (W) for at least 30 minutes. To provide equilibrium between adsorption and desorption on the sample surfaces the gas injection system (GIS) valves were opened for at least 3 minutes before the patterning processes. Chamber pressures were 6×10^{-6} mbar and 1×10^{-6} mbar before and 2×10^{-5} mbar and 1.5×10^{-5} mbar after valve opening in Austria and the US, respectively. The working distance during deposition for experiments performed in Austria was at 5 mm according to the eucentric height, while deposition in the US was performed with a working distance of 6 mm due to the location of the GIS nozzles. S16 summarizes in table form further experimental details including the GIS nozzle positions and angles for the different microscopes and precursors. Electron beam optimization was carefully done on a pre-deposited dot followed by beam blanking and stage moves towards real deposition areas in close proximity. To prevent any further mechanical drift a waiting period of about 10 minutes was introduced before deposition. Patterning was performed using stream files which allow precise process control. Subsequent

electron imaging was done at low dose and in 52° stage tilt position after a waiting period of more than 30 minutes to enable desorption of precursor molecules.

Atomic force microscopy was performed using a Dimension 3100 AFM (Bruker Nano) with a Nanoscope IVa controller and a XYZ Hybrid scan head in tapping mode using Olympus OMCL TS-240 AFM tips. Details on the fabrication process of the spiral out pad in figure 2(d) are given in ²⁴.

Figure 6 provides an abbreviated flow diagram for the 3D FEBID simulation. Lastly, a complete table of simulation parameters is provided in Table 1.

Acknowledgments

JDF and PDR acknowledge that the creation of the model and simulation were conducted at the Center for Nanophase Materials Sciences, which is a DOE Office of Science User Facility. RW and HP gratefully acknowledge the valuable support provided from Prof. Dr. Ferdinand Hofer. RW and HP also acknowledge financial support by the COST action CELINA (Nr. CM1301), EUROSTARS project TRIPLE-S (Nr. E! 8213) and the bmvit exchange program. MGS acknowledges support from the National Defense Science and Engineering Graduate Fellowship funded through the AFOSR. BBL acknowledges support via the University of Tennessee Chancellor's Fellowship program.

Supporting Information. (S1) Three-dimensional rendering of deposits and movie, (S2) The cut-off energy used in the Monte Carlo electron scattering simulation, (S3) Monte Carlo electron trajectory mapping to 3D deposits, (S4) Electron interaction volume creation, (S5) The surface area of surface voxels, (S6) Deposit surface normal estimation and surface orientation dependent surface flux, (S7) 3D FEBID simulation calibration factor, (S8) FEBID parameters, (S9) Comparison of 3D FEBID simulation results with a previous 2D FEBID simulation, (S10) 3D FEBID simulations of published work I; sample current monitor, (S11) 3D FEBID simulations of published work II; low angle segments (S12) Movie of the beam dwell pattern for a 3D vertical square frame, (S13) Movie of 3D FEBID simulation results for vertical square frame, (S14) Virtual SEM images of 3D FEBID simulation results, (S15) Movies of 3D FEBID simulation of a vertical, vertex standing cube and a virtual SEM rotation around the deposited cube, (S16) Various experimental FEBID conditions

Figure Captions

Figure 1 (a) 3D FEBID (focused electron beam–induced deposition) simulation results for the ‘segment’ geometry. The beam energy was 30 keV, the beam current was 21 pA and the FWHM of the electron beam was 4 nm. The colormap reflects the precursor molecule coverage for the case of a partially directed gas beam (20 mTorr, indicated as gas flux vector) and a

purely diffuse component of (10 mTorr). Precursor coverage is relatively lower in the shadow cast by the segment terminated pillar because the directed gas flux is blocked. More details are provided in S1. (b) A Monte Carlo simulation of an electron trajectory immersed in an infinite 3D solid using a point source beam (δ). (c) The electron trajectory in (b) is adapted to the 3D deposit geometry for FEBID. Adaption includes accounting for the real Gaussian beam shape as well as transport through vacuum in which no scattering occurs. (d) The multi-length scale nature of the simulation. (1) The image pixel size reflects the simulation voxel size of 8 nm, (2) a simulated deposit (white) and (3) primary electron trajectories (green) for the geometry described in (c) for the beam energy of 30 keV. The scale on the graph applies also to the image. (e) Simulation illustrating the precursor coverage for a precursor flux with directed and diffuse components on a surface with an arbitrary topology. The ‘mountain range’ morphology highlights the expected shadowing pattern for a purely directed precursor flux.

Figure 2 (a) A spatial map in the x–y plane of primary electron beam shots for a spiral–out scanning strategy²⁴. The projection of the gas flux vector in the xy–plane is shown. An AFM image shows the experimental result for this scanning strategy ($E_0=5$ keV, $i_b=400$ pA, $r_b=27.1$ nm, $\Lambda=13$ nm, $\alpha=15^\circ$, $\beta=52^\circ$). The edge length of the prism is 2 μ m. Ledge #1 is 62 nm high while ledge #3 is 42 nm high. (b) The complementary simulation of filled voxels yields a similar morphology. However, the voxel size of 8 nm impairs the resolution. The bottom of (b) represents a 3x3, vertical slice through the prism revealing partially filled surface voxels where the fraction and colormap indicate the volume fraction of deposit. (c) Sub-voxel resolution is estimated/recovered by executing a summation operation of total deposition in the z–direction; the direction of the FEBID growth front for this geometry. Above (c) is the summation of the 3x3 voxel array in the vertical/z-dimension (d) A high-resolution 3D AFM image of the complementary, experimentally derived thin film prism.

Figure 3 An experimental study of segment angle (ζ°) vs beam dwell time for PtC₅ deposited from the MeCp(Pt^{IV})Me₃ precursor. After an initial constant pillar growth, the beam is scanned with a pixel point pitch (Λ) fixed at 1 nm and the scan length was 400 nm. The beam dwell time (τ_d) is superimposed over the SEM image for each segment in units of milliseconds. The bottom left insets shows AuC_x and WC_x segments, derived from the precursors (dimethylgold acetylacetonate) and (tungsten hexacarbonyl), for a dwell time of 39 ms ($\Lambda = 1$ nm).

Figure 4 (a) A simulated segment grown at 30 keV and 21 pA with a dwell time per pixel of 11 ms and 1 nm pixel point pitch. The 3D object was grown in two steps: a static dwell of 1.75 s followed to generate the vertical pedestal followed by a line scan in the x–y plane to create segment characterized by a beam speed of 9.1×10^{-2} nm/ms. The inset shows a top–down image of the segment. The pixel size in the image is 8 nm and equal to the simulation voxel size. (b) Simulated (grey) and experimental results (red) for the segment angle (in degrees) as a function of beam dwell time. (c) Consistent with experiments, simulations revealed that the segment angle variation with respect to segment growth direction relative to the gas flux vector (α) was negligible. (d) FEBID design for a tilted square frame with segments labeled. Projections of the frame on the x-y, y-z, x-z planes are shown in grey for 3D clarity. The temporal distribution of beam dwell positions is shown in the movie file in S12. A movie of the

FEBID growth is provided in S13 and a virtual SEM image of the simulated result is provided in (e) (see S14 for virtual SEM method). The snapshot in (e) was taken at an angle of 52° with respect to the virtual substrate normal and was stretched by a factor of $1/\sin(52^\circ)$ in the vertical direction to mimic (f) the tilted experimental SEM image. The scale bars in (e) and (f) are 200 nm.

Figure 5 (a) SEM image of FEBID growth of a cubic frame. The segment length was 200 nm and the cubic frame was rotated vertically by 54.7° . The rotation made all segment angles equal at 35.3° requiring a dwell time (τ_d) of 11.0 ms at a pixel point pitch (Λ) of 1 nm. 2008 individual pixel dwells were required to write the cubic mesh. The colormap is normalized to the z-coordinate. (b) The virtual SEM image of the simulation results that mimics the experiment in (a). (c) The simulation results rendered in the form of deposit surface voxels where the colormap is linked to the vertical, z-coordinate (see S15 for FEBID movie) (d) A segment slice, deposited using $\tau_d=2.4$ ms and $\Lambda=0.2$ nm, showing the history of the deposited voxels based on SEs generated from first scattering step of an electron (SE^A). (e) On the other hand secondary electrons generated beyond the first scattering event (SE^B s) dominate the segment thickness due to transmitted primary electrons. Also, the substrate staining is caused mostly SE^B s with little contribution from SE^A s. (f) A slice through the full 3D segment morphology where half the structure has been removed to reveal the interior. The colormap in this case reveals the fraction of SE^A and SE^B (where $SE^B = 1-SE^A$) contribution on the same plot. (g) A 3D truncated icosahedron deposited by FEBID with a characteristic edge dimension of 200 nm. The SEM image was acquired at 0° tilt in the top down configuration. The truncated icosahedron design with a bottom hexagon was rotated 15° off the substrate plane on one of the hexagon vertices. The comparable simulated results are shown in (h) and (i).

Figure 6 The hybrid Monte Carlo–continuum 3D focused electron beam–induced deposition simulation execution flow diagram.

Table 1 Variables critical to the simulation including materials properties, electron beam settings and precursor properties.

References

1. van Dorp, W. F. Sub-10 nm Writing: Focused Electron Beam-Induced Deposition in Perspective. *Appl. Phys. A: Mater. Sci. Process.* **2014**, 117, 1615-1622.
2. van Dorp, W. F.; Zhang, X. Y.; Feringa, B. L.; Hansen, T. W.; Wagner, J. B.; Hosson, J. T. M. Molecule-by-Molecule Writing Using a Focused Electron Beam. *ACS Nano* **2012**, 6, 10076-10081.
3. Esposito, M.; Tasco, V.; Cuscuna, M.; Todisco, F.; Benedetti, A.; Tarantini, I.; De Giorgi, M.; Sanvitto, D.; Passaseo, A. Nanoscale 3D Chiral Plasmonic Helices with Circular Dichroism at Visible Frequencies. *ACS Photonics* **2015**, 2, 105-114.
4. Fisher, J. S.; Kottke, P. A.; Kim, S.; Federov, A. G. Rapid Electron Beam Writing of Topologically Complex 3D Nanostructures using Liquid Phase Precursor. *Nano Lett.* **2015**, 15, 8385-8391.

5. Kretz, J.; Rudolph, M.; Weber, M.; Koops, H. W. P. 3-Dimensional Structurization by Additive Lithography, Analysis of Deposits using TEM and EDX, and Application to Field-Emitter Tips. *Microelectron. Eng.* **1994**, 23, 477-481.
6. Koops, H. W. P.; Kaya, A.; Weber, M. Fabrication and Characterization of Platinum Nanocrystalline Material grown by Electron-Beam Induced Deposition. *J. Vac. Sci. Technol. B* **1995**, 13, 2400-2403.
7. Gazzadi, G. C.; Frabboni, S.; Menozzi, C. Suspended Nanostructures grown by Electron Beam-Induced Deposition of Pt and TEOS Precursors. *Nanotechnology* **2007**, 18, 445709
8. Molhave, K.; Madsen, D. N.; Dohn, S.; Boggild, P. Constructing, Connecting and Soldering Nanostructures by Environmental Electron Beam Deposition. *Nanotechnology* **2004**, 15, 1047-1053.
9. Hoflich, K.; Yang, R. B.; Berger, A.; Leuchs, G.; Christiansen, S. The Direct Writing of Plasmonic Gold Nanostructures by Electron-Beam-Induced Deposition. *Adv. Mater.* **2011**, 23, 2657-2661.
10. Koops, H. W. P.; Hoinkis, O. E.; Honsberg, M. E. W.; Schmidt, R.; Blum, R.; Bottger, G.; Kuligk, A.; Liguda, C.; Eich, M. Two-Dimensional Photonic Crystals produced by Additive Nanolithography with Electron Beam-Induced Deposition act as Filters in the Infrared. *Microelectron. Eng.* **2001**, 57-8, 995-1001.
11. Utke, I. *Nanofabrication Using Focused Ion and Electron Beams, Principles and Applications*. Oxford University Press: **2012**.
12. Floreani, F.; Koops, H. W.; Elsasser, W. Operation of High Power Field Emitters Fabricated with Electron Beam Deposition and Concept of a Miniaturised Free Electron Laser. *Microelectron Eng* **2001**, 57-8, 1009-1016.
13. Matsui, S.; Kaito, T.; Fujita, J.; Komuro, M.; Kanda, K.; Haruyama, Y. Three-Dimensional Nanostructure Fabrication by Focused-Ion-Beam Chemical Vapor Deposition. *J. Vac. Sci. Technol. B* **2000**, 18, 3181-3184.
14. Matsui, S. Focused-Ion-Beam Deposition for 3-D Nanostructure Fabrication. *Nucl. Instrum. Methods Phys. Res., Sect. B* **2007**, 257, 758-764.
15. Smith, D. A.; Fowlkes, J. D.; Rack, P. D. A Nanoscale Three-Dimensional Monte Carlo Simulation of Electron-Beam-Induced Deposition with Gas Dynamics. *Nanotechnology* **2007**, 18, 265308
16. Plank, H.; Smith, D. A.; Haber, T.; Rack, P. D.; Hofer, F. Fundamental Proximity Effects in Focused Electron Beam Induced Deposition. *ACS Nano* **2012**, 6, 286-294.
17. Smith, D. A.; Fowlkes, J. D.; Rack, P. D. Simulating the effects of surface diffusion on electron beam induced deposition via a three-dimensional Monte Carlo simulation. *Nanotechnology* **2008**, 19, 415704
18. Fowlkes, J. D.; Rack, P. D. Fundamental Electron-Precursor-Solid Interactions Derived from Time-Dependent Electron-Beam-Induced Deposition Simulations and Experiments. *ACS Nano* **2010**, 4, 1619-1629.
19. Rykaczewski, K.; White, W. B.; Fedorov, A. G. Analysis of Electron Beam Induced Deposition (EBID) of Residual Hydrocarbons in Electron Microscopy. *J Appl. Phys.* **2007**, 101, 054307.
20. Toth, M.; Lobo, C.; Friedli, V.; Szkudlarek, A.; Utke, I. Continuum Models of Focused Electron Beam Induced Processing. *Beilstein J. Nanotech.* **2015**, 6, 1518-1540.
21. Lobo, C. J.; Toth, M.; Wagner, R.; Thiel, B. L.; Lysaght, M. High Resolution Radially Symmetric Nanostructures from Simultaneous Electron Beam Induced Etching and Deposition. *Nanotechnology* **2008**, 19, 025303.
22. Winkler, R.; Geier, B.; Plank, H. Spatial Chemistry Evolution during Focused Electron Beam-Induced Deposition: Origins and Workarounds. *Appl. Phys. A: Mater. Sci. Process.* **2014**, 117, 1675-1688.

23. Winkler, R.; Szkudlarek, A.; Fowlkes, J. D.; Rack, P. D.; Utke, I.; Plank, H. Toward Ultraflat Surface Morphologies During Focused Electron Beam Induced Nanosynthesis: Disruption Origins and Compensation. *ACS Appl. Mater. Interfaces* **2015**, *7*, 3289-3297.
24. Winkler, R.; Fowlkes, J.; Szkudlarek, A.; Utke, I.; Rack, P. D.; Plank, H. The Nanoscale Implications of a Molecular Gas Beam during Electron Beam Induced Deposition. *ACS Appl. Mater. Interfaces* **2014**, *6*, 2987-2995.
25. Cullen, J.; Bahm, A.; Lobo, C. J.; Ford, M. J.; Toth, M. Localized Probing of Gas Molecule Adsorption Energies and Desorption Attempt Frequencies. *J. Phys. Chem. C* **2015**, *119*, 15948-15953.
26. Fowlkes, J. D.; Geier, B.; Lewis, B. B.; Rack, P. D.; Stanford, M. G.; Winkler, R.; Plank, H. Electron Nanoprobe Induced Oxidation: a Simulation of Direct-Write Purification. *Phys. Chem. Chem. Phys.* **2015**, *17*, 18294-18304.
27. Joy, D. C. An Introduction to Monte-Carlo Simulations. *Scanning Microscopy* **1991**, *5*, 329-337.
28. Lin, Y.; Joy, D. C. A New Examination of Secondary Electron Yield Data. *Surface and Interface Analysis* **2005**, *37*, 895-900.
29. Bret, T.; Utke, I.; Hoffmann, P. Influence of the Beam Scan Direction during Focused Electron Beam Induced Deposition of 3D Nanostructures. *Microelectron. Eng.* **2005**, *78-79*, 307-313.
30. Friedli, V.; Utke, I. Optimized Molecule Supply from Nozzle-based Gas Injection Systems for Focused Electron- and Ion-Beam Induced Deposition and Etching: Simulation and Experiment. *J. Phys. D: Appl. Phys.* **2009**, *42*, 125305.
31. Cullen, J.; Lobo, C. J.; Ford, M. J.; Toth, M. Electron-Beam-Induced Deposition as a Technique for Analysis of Precursor Molecule Diffusion Barriers and Prefactors. *ACS Appl. Mater. Interfaces* **2015**, *7*, 21408-21415.
32. Friedli, V.; Santschi, C.; Michler, J.; Hoffmann, P.; Utke, I. Mass Sensor for *in situ* Monitoring of Focused Ion and Electron Beam Induced Processes. *Appl. Phys. Lett.* **2007**, *90*, 053106.
33. Silvis-Cividjian, N.; Hagen, C. W.; Leunissen, L. H. A.; Kruit, P. The Role of Secondary Electrons in Electron-Beam-Induced-Deposition Spatial Resolution. *Microelectron. Eng.* **2002**, *61-62*, 693-699.
34. Utke, I.; Hoffmann, P.; Melngailis, J. Gas-Assisted Focused Electron Beam and Ion Beam Processing and Fabrication. *J. Vac. Sci. Technol. B* **2008**, *26*, 1197-1276.
35. van Dorp, W. F. The Role of Electron Scattering in Electron-Induced Surface Chemistry. *Phys. Chem. Chem. Phys.* **2012**, *14*, 16753-16759.
36. Schmied, R.; Froch, J. E.; Orthacker, A.; Hobisch, J.; Trimmel, G.; Plank, H. A Combined Approach to Predict Spatial Temperature Evolution and its Consequences during FIB Processing of Soft Matter. *Phys. Chem. Chem. Phys.* **2014**, *16*, 6153-6158.
37. Arnold, G.; Timilsina, R.; Fowlkes, J.; Orthacker, A.; Kothleitner, G.; Rack, P. D.; Plank, H. Fundamental Resolution Limits during Electron-Induced Direct-Write Synthesis. *ACS Appl. Mater. Interfaces* **2014**, *6*, 7380-7387.
38. Kometani, R.; Warisawa, S.; Ishihara, S. The 3D Nanostructure Growth Evaluations by the Real-Time Current Monitoring on Focused-Ion-Beam Chemical Vapor Deposition. *Microelectron. Eng.* **2010**, *87*, 1044-1048.
39. Botman, A.; Mulders, J. J. L.; Weemaes, R.; Mentink, S. Purification of Platinum and Gold Structures after Electron-Beam-Induced Deposition. *Nanotechnology* **2006**, *17*, 3779-3785.
40. Bret, T.; Utke, I.; Hoffmann, P.; Abourida, M.; Doppelt, P. Electron Range Effects in Focused Electron Beam Induced Deposition of 3D Nanostructures. *Microelectron. Eng.* **2006**, *83*, 1482-1486.
41. Bret, T.; Utke, I.; Gaillard, C.; Hoffmann, P. Periodic Structure Formation by Focused Electron-Beam-Induced Deposition. *J. Vac. Sci. Technol. B* **2004**, *22*, 2504-2510.
42. Hamilton, B.; Bilbao, S. Hexagonal vs. Rectilinear Grids for Explicit Finite Difference Schemes for the Two-Dimensional Wave equation. *J. Acoust. Soc. Am.* **2013**, *133*, 015120.

43. Geier, B.; Gspan, C.; Winkler, R.; Schmied, R.; Fowlkes, J. D.; Fitzek, H.; Rauch, S.; Rattenberger, J.; Rack, P. D.; Plank, H. Rapid and Highly Compact Purification for Focused Electron Beam Induced Deposits: A Low Temperature Approach Using Electron Stimulated H₂O Reactions. *J. Phys. Chem. C* **2014**, 118, 14009-14016.

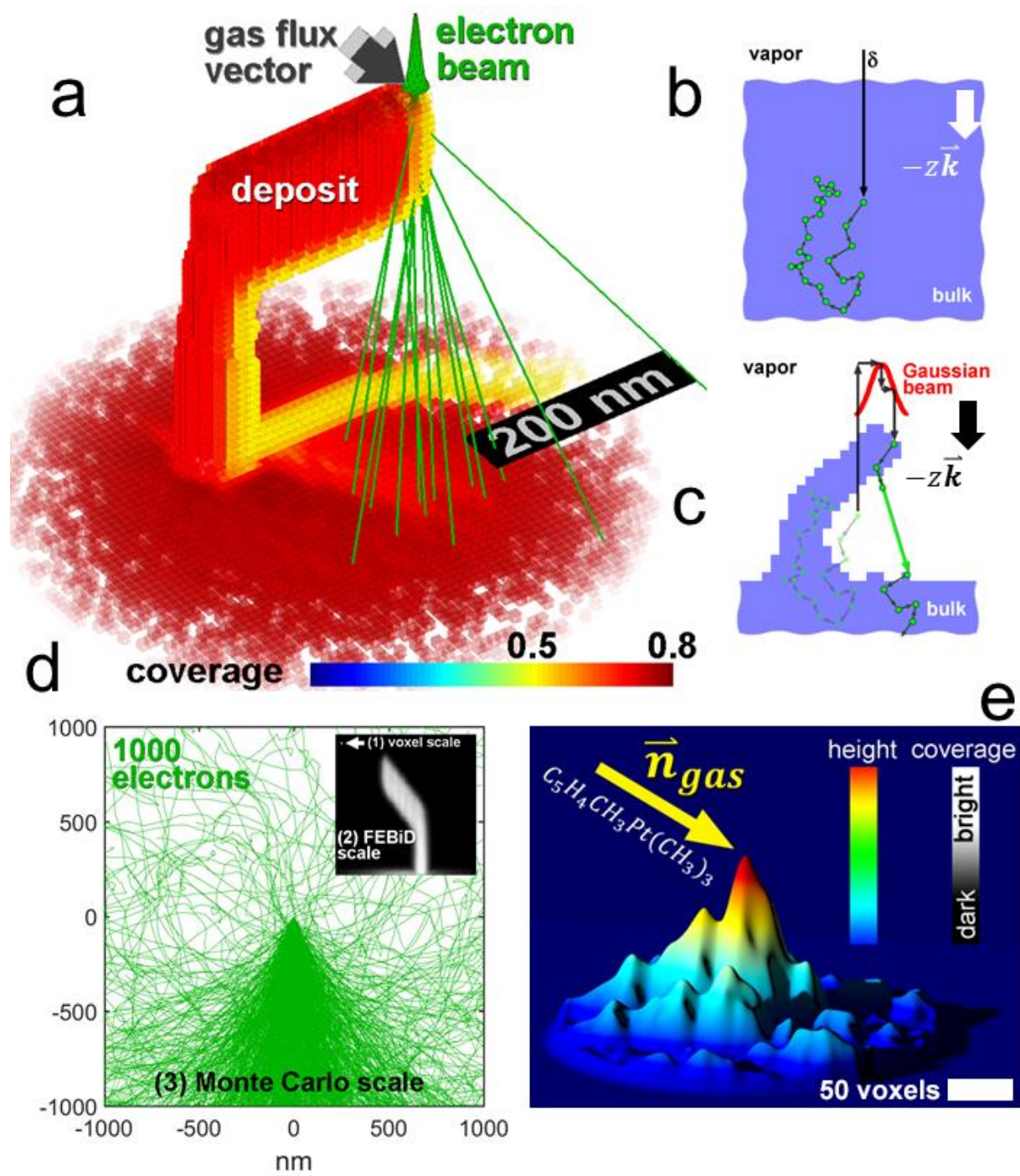


Figure 1

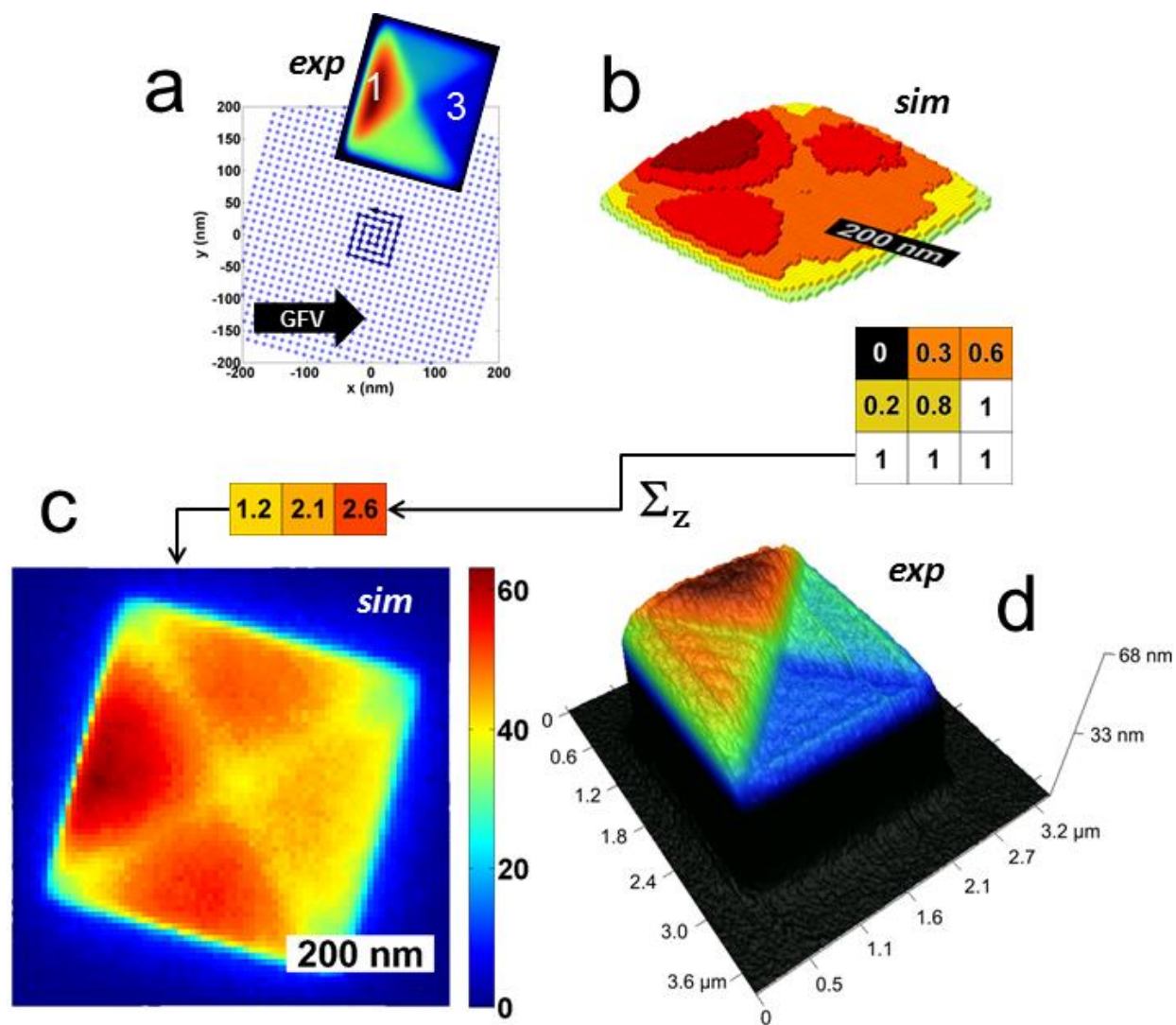


Figure 2

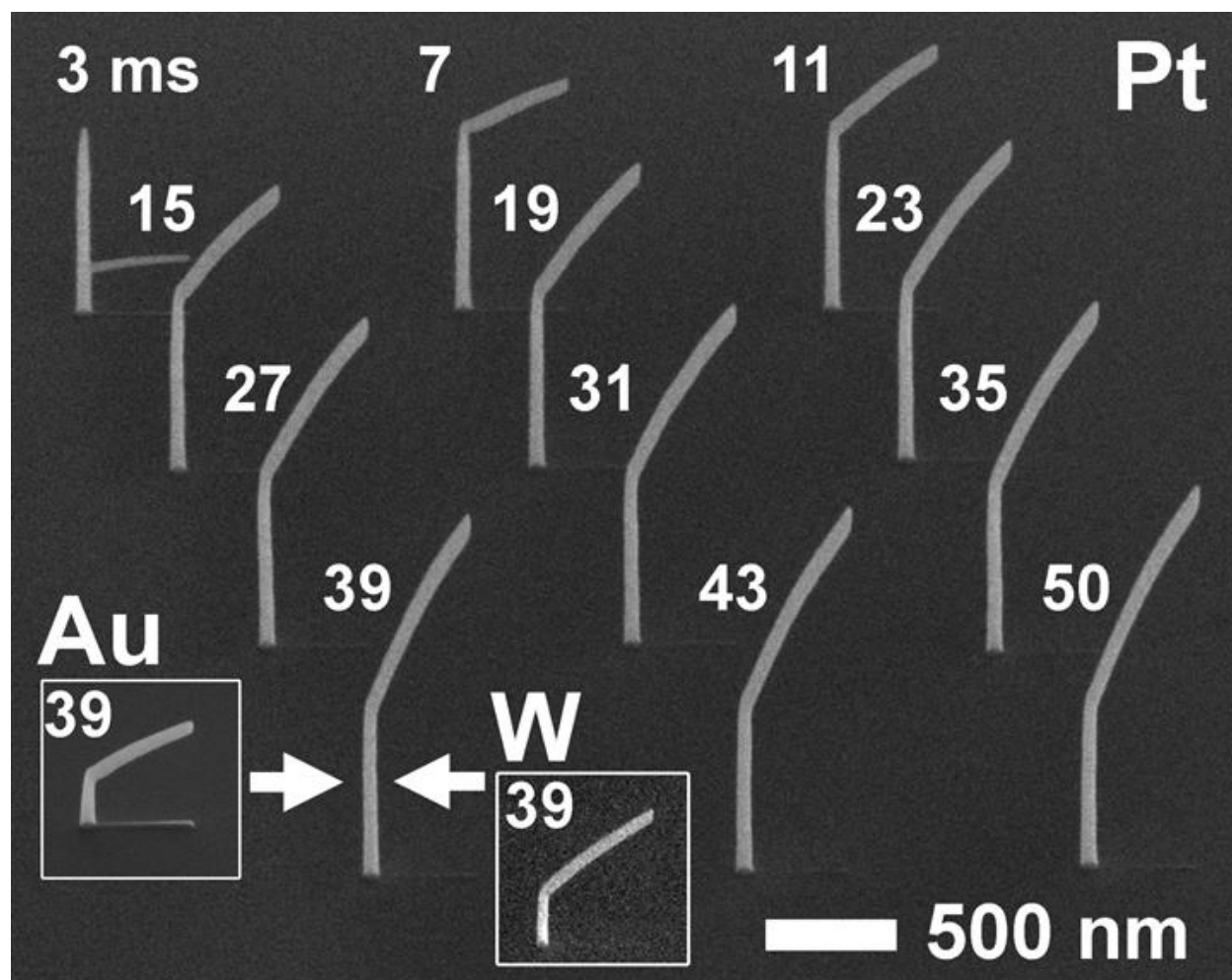


Figure 3

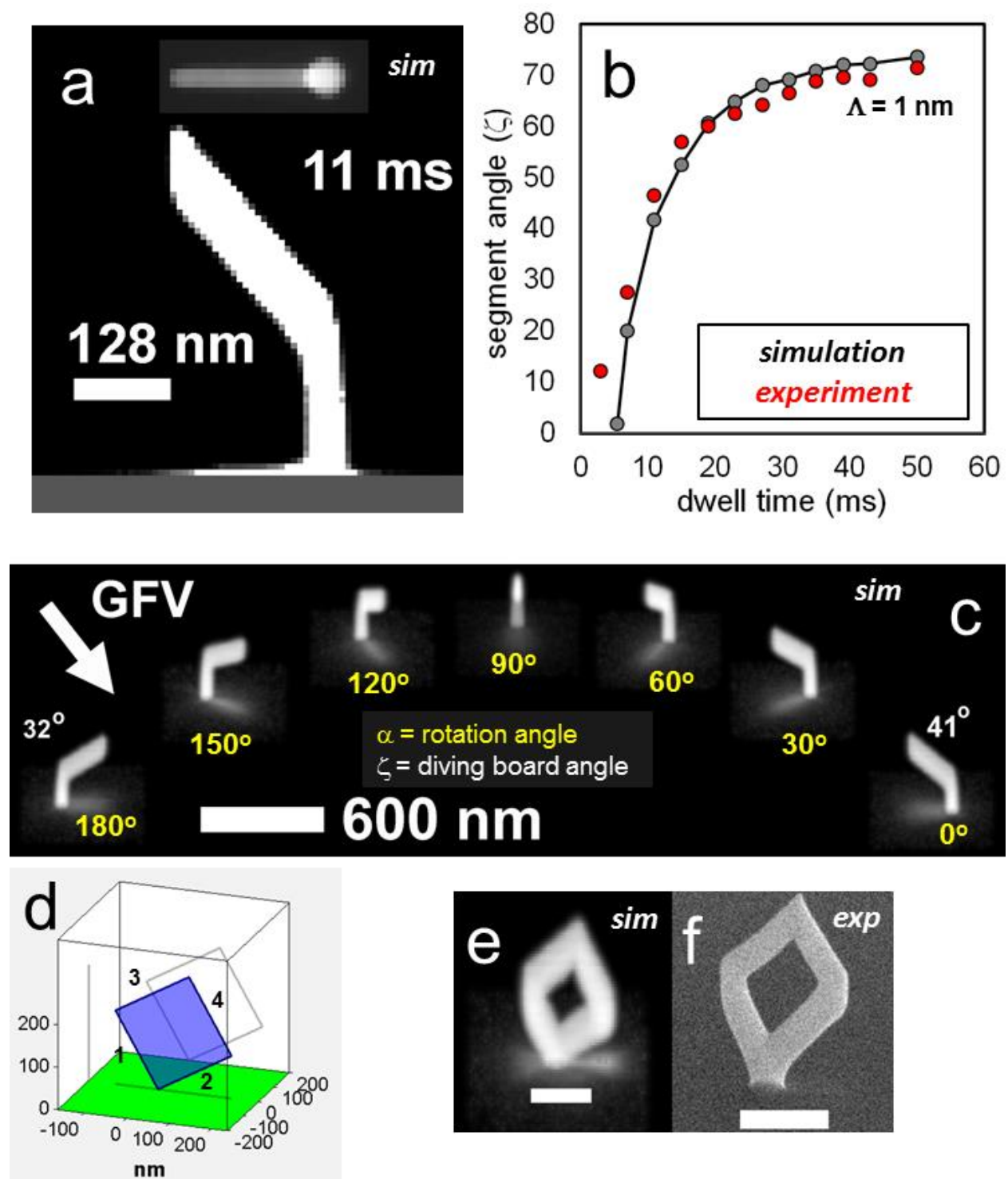


Figure 4

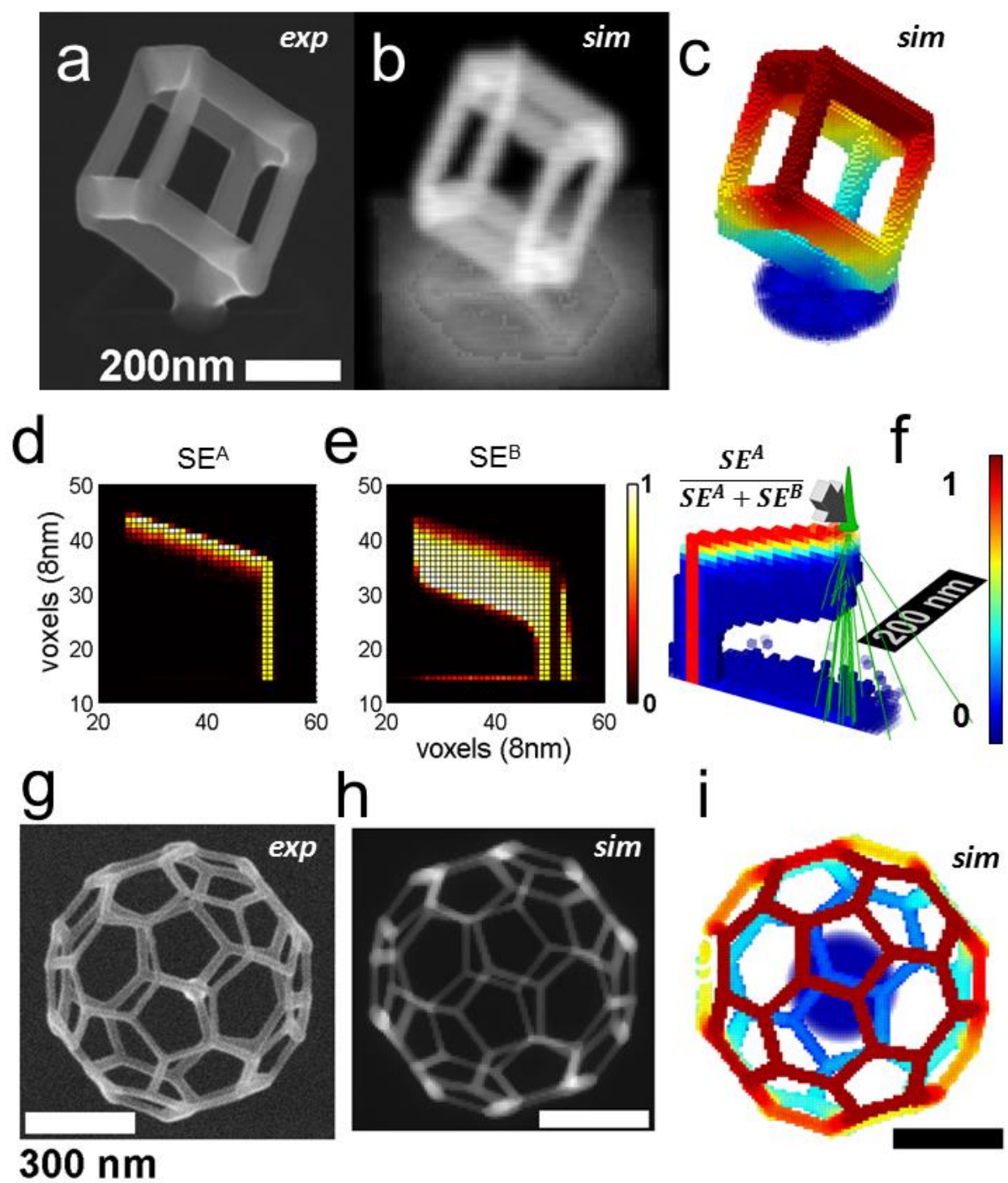


Figure 5

Table of variables

$E_o = 30$; primary electron beam energy [keV]

$i_o = 21$; primary electron beam current $\left[\frac{C}{s}\right]$

$FWHM = 4$; focused electron beam size [nm]

$\tau_d = 3 - 50$; electron beam dwell time per pixel [s]

$\Lambda = 1$; pixel point pitch [nm]

$v = 0.02 - 0.2$; electron beam speed $\left[\frac{nm}{s}\right]$

$D = 0.4$; diffusion coefficient of $MeCpPt^{IV}Me_3$ $\left[\frac{\mu m^2}{s}\right]$

$P = 30$; gas pressure at the deposit surface [mTorr]

$P_{beam} = 20$; specular component of total pressure [mTorr]

$P_b = 10$; diffuse component of total pressure [mTorr]

$\tau = 100$; mean residence time of $MeCpPt^{IV}Me_3$ [μs]

$\delta = 1$; sticking probability of $MeCpPt^{IV}Me_3$ on PtC_5 [0 – 1]

$\sigma = 0.013$; mean, total dissociation cross – section for $MeCpPt^{IV}Me_3$ [nm^2]

$\varepsilon = 73$; energy required to create a secondary electron in PtC_5 [eV]

$f_{SE} = 1$; fraction of inelastic energy for secondary electron creation [0 – 1]

$\lambda = 2.5$; mean free path of a secondary electron in PtC_5 [nm]

$s_p = 2.8$; surface density density for $MeCpPt^{IV}Me_3$ adsorption $\left[\frac{sites}{nm^2}\right]$

$s_d = 4.8$; PtC_5 deposit density $\left[\frac{molecules}{nm^2}\right]$

$\chi = 2.1$; residual fitting parameter for the FEBID simulation

$\alpha = 0 - 180^\circ$; angle between beam scanning vector and gas flux vector projected on the substrate

$\beta = 52^\circ$; angle between substrate surface and gas nozzle axis

$\xi = 0 - 90^\circ$; segment angle with respect to the substrate plane

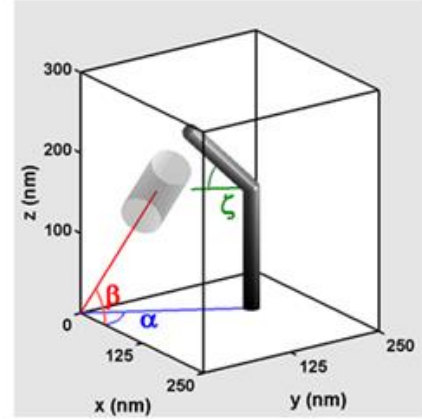


Table 1

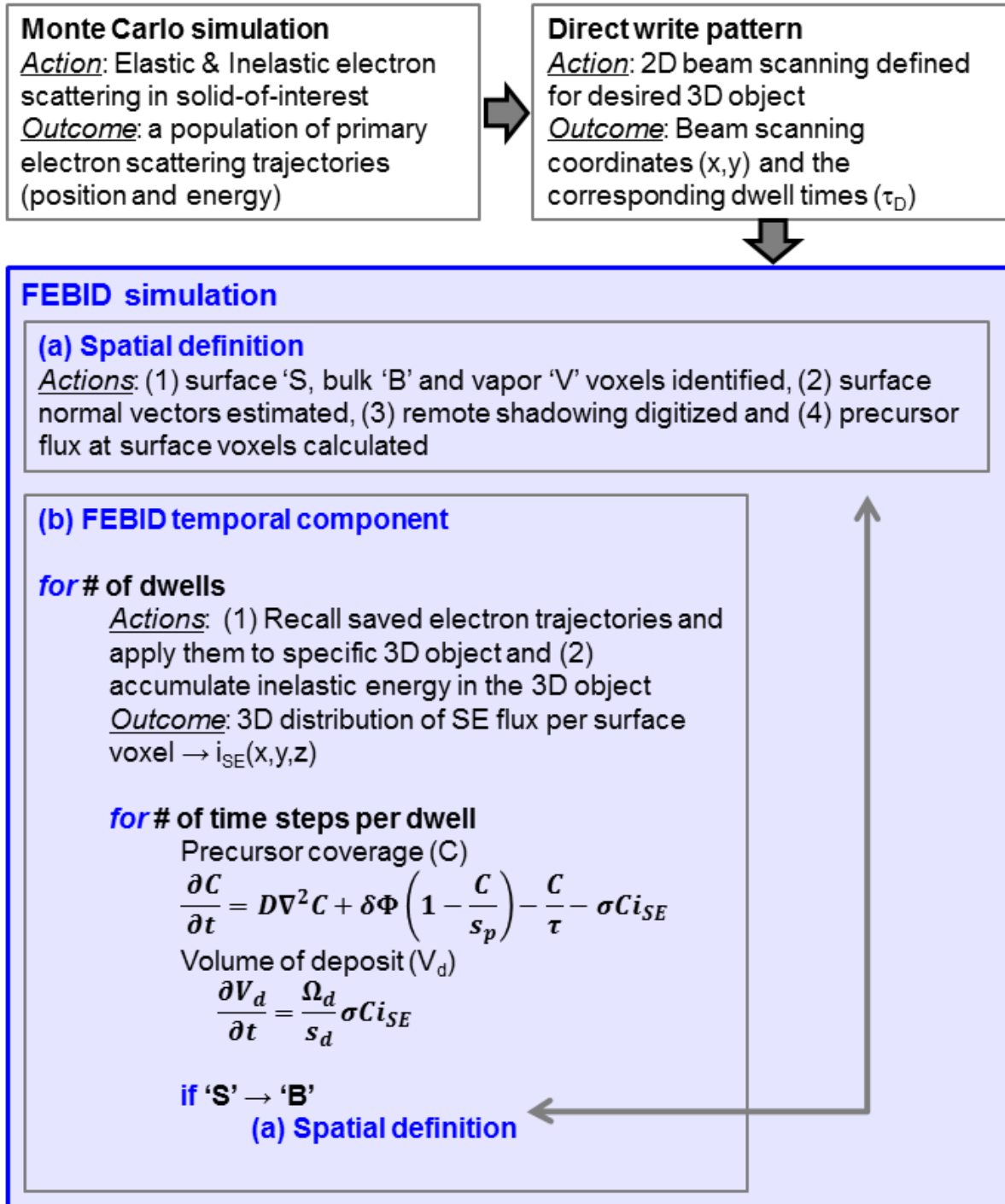


Figure 6

