Supporting Information

3D Nanoprinting Replication Enhancement using a Simulation Informed, Analytical Model for Electron Beam Exposure Dose Compensation

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Supporting Information 1: Details on simulation parameters for Figure 3, 4, 6, 7, 13, 14 and details on experimental parameters for Figure 10 - 12, 15 – 18.

Experimental and simulation parameters are reported for each Figure that displays such information.

Table S1. Simulation parameters for Figure 3a

Parameter	Definition	Values	Units
$\boldsymbol{E}$	Electron beam energy	30	keV
$\boldsymbol{i_b}$	Electron beam current	35	pA
$\boldsymbol{r_b}$	Electron beam (FWHM)	6.25	nm
$\boldsymbol{PtC_x}$	Deposit composition (Pt nanoparticles in C matrix)	PtC_8	
$\boldsymbol{\Phi}$	Precursor impingement flux	1758	$/nm^2 s$
$\boldsymbol{\Omega}$	Molecular volume (deposit)	0.175	nm^3
$\boldsymbol{s_d}$	Deposit surface density	3.20	$/nm^2$
$\boldsymbol{k}$	Thermal conductivity	0.16	$W/m\,K$
$\boldsymbol{P}$	Precursor pressure at the BIR	0.6	$mTorr$

Simulation Input in addition to the constants listed in Table 2

Pixel exposure time (setting) & resulting segment angle (simulation)

$\boldsymbol{\tau_d\ (ms)}$	$\boldsymbol{\zeta}$
9.638	53.0

Table S2. Simulation parameters for Figure 3b

Parameter	Definition	Values	Units
$\boldsymbol{E}$	Electron beam energy	10	keV
$\boldsymbol{i_b}$	Electron beam current	48	pA
$\boldsymbol{r_b}$	Electron beam (FWHM)	7.2	nm
$\boldsymbol{PtC_x}$	Deposit composition (Pt nanoparticles in C matrix)	$PtC_{6.32}$	
$\boldsymbol{\Phi}$	Precursor impingement flux	1758	$/nm^2 s$
$\boldsymbol{\Omega}$	Molecular volume (deposit)	0.141	nm^3
$\boldsymbol{s_d}$	Deposit surface density	3.68	$/nm^2$
$\boldsymbol{k}$	Thermal conductivity	0.20	$W/m\,K$
$\boldsymbol{P}$	Precursor pressure at the BIR	0.60	$mTorr$

Simulation Input in addition to the constants listed in Table 2

Pixel exposure time (setting) & resulting segment angle (simulation)

$\boldsymbol{\tau_d\ (ms)}$	$\boldsymbol{\zeta}$
5.342	49.2

Table S3. Simulation parameters for Figures 4, 6, 7

Parameter	Definition	Values	Units
$\boldsymbol{E}$	Electron beam energy	30	keV
$\boldsymbol{i_b}$	Electron beam current	35	pA
$\boldsymbol{r_b}$	Electron beam (FWHM)	6.5	nm
$\boldsymbol{PtC_x}$	Deposit composition (Pt nanoparticles in C matrix)	PtC_8	
$\boldsymbol{\Phi}$	Precursor impingement flux	1758	$/nm^2 s$
$\boldsymbol{\Omega}$	Molecular volume (deposit)	0.175	nm^3
$\boldsymbol{s_d}$	Deposit surface density	3.20	$/nm^2$
$\boldsymbol{k}$	Thermal conductivity (30 keV)	0.16	$W/m\,K$
$\boldsymbol{P}$	Precursor pressure at the BIR	0.60	$mTorr$

Simulation Input in addition to the constants listed in Table 2

Table S4. Experimental parameters for Figure 10 <E_{30},i_{35}>

Parameter	Definition	Values	Units
$\boldsymbol{E}$	Electron beam energy	30	keV
$\boldsymbol{i_b}$	Electron beam current	35	pA
$\boldsymbol{r_b}$	Electron beam size (full–width at half–maximum)	3.8	nm
$\boldsymbol{\Lambda}$	Exposure pixel point pitch	1	nm
$\boldsymbol{A_xB_y}$	Substrate composition	$SiO_2(5\,nm)/Si$	[ ]

Pixel exposure time (setting) & resulting segment angle (Experimental)

$\boldsymbol{\tau_d\ (ms)}$	$\boldsymbol{\zeta}$
4.792	22.7

Table S5. DBEA & TCN Parameters

Parameter	Definition	Values	Units
f_a	Fraction of absorption path through deposit	1.10	[ ]
δ_I	SE(I) yield per PE	0.35	[ ]
Δs	Span of concentration gradient in the BIR	80	nm
P	Precursor pressure (@ BIR)	0.50	$mTorr$
T_o	Substrate temperature	294	K

Pixel exposure time (setting) & resulting segment angle (Experimental)

$\tau_{d,o}$ (ms)	ζ
4.792	24.6

Table S6. Experimental parameters for Figure 11a <E_{30},i_{35}>

Parameter	Definition	Values	Units (*)
E	Electron beam energy	30	keV
i_b	Electron beam current	35	pA
r_b	Electron beam size (full–width at half–maximum)	3.8	nm
Λ	Exposure pixel point pitch	1	nm
A_xB_y	Substrate composition	$SiO_2(5\ nm)/Si$	[ ]
T_o	Substrate temperature	294	K

Pixel exposure time (setting) & resulting segment angle (Experimental, No DBEA) (Figure 11a)

τ_d (ms)	ζ
4.792	20.1
5.349	28.7
7.164	35.9
9.386	52.1
12.670	58.7
21.060	69.5

Table S7. DBEA Parameters (Figure 11b)

Parameter	Definition	Values	Units (*)
f_a	Fraction of absorption path through deposit	0.95	[ ]
δ_I	SE(I) yield per PE	0.35	[ ]
Δs	Span of concentration gradient in the BIR	80	nm
P	Precursor pressure (@ BIR)	0.60	$mTorr$
T_o	Substrate temperature	294	K

Pixel exposure time (setting) & resulting segment angle (Experimental, DBEA) (Figure 11b)

$\tau_{d,o}$ (ms)	ζ
4.792	23.8
5.349	27.1
7.164	38.6
9.386	52.0
12.670	60.8
21.060	71.2

Figures 11e–f → see Figure 10 conditions

Table S8. Figure 12: Experimental parameters for Figure 12a <E_{10},i_{48}>

Parameter	Definition	Values	Units (*)
$\boldsymbol{E}$	Electron beam energy	10	keV
$\boldsymbol{i_b}$	Electron beam current	48	pA
$\boldsymbol{r_b}$	Electron beam size (full–width at half–maximum)	7.2	nm
$\boldsymbol{\Lambda}$	Exposure pixel point pitch	1	nm
$\boldsymbol{A_xB_y}$	Substrate composition	$SiO_2(5\,nm)/Si$	[ ]
$\boldsymbol{T_o}$	Substrate temperature	294	K

Pixel exposure time (setting) & resulting segment angle (Experimental, no DBEA) (Figure 12a)

$\boldsymbol{\tau_d\ (ms)}$	$\boldsymbol{\zeta}$
2.419	22.5
3.435	36.0
4.020	40.6
5.342	46.8
8.710	59.5
17.530	69.8

Table S9. DBEA Parameters for Figure 12b

Parameter	Definition	Values	Units (*)
$\boldsymbol{f_a}$	Fraction of absorption path through deposit	0.53	[ ]
$\boldsymbol{\delta_I}$	SE(I) yield per PE	0.65	[ ]
$\boldsymbol{\Delta s}$	Span of concentration gradient in the BIR	80	nm
$\boldsymbol{P}$	Precursor pressure (@ BIR)	0.65	$mTorr$
$\boldsymbol{T_o}$	Substrate temperature	294	K

Pixel exposure time (setting) & resulting segment angle (Experimental, DBEA) (Figure 12b)

$\boldsymbol{\tau_{d,o}\ (ms)}$	$\boldsymbol{\zeta}$
2.419	19.3
3.435	33.9
4.020	42.8
5.342	49.0
8.710	60.2
17.530	70.9

Table S10. Microscope Parameters for Figure 12e

Parameter	Definition	Values	Units (*)
$\boldsymbol{E}$	Electron beam energy	10	keV
$\boldsymbol{i_b}$	Electron beam current	48	pA
$\boldsymbol{r_b}$	Electron beam size (full–width at half–maximum)	7.2	nm
$\boldsymbol{\Lambda}$	Exposure pixel point pitch	1	nm
$\boldsymbol{A_xB_y}$	Substrate composition	$SiO_2(5\,nm)/Si$	[ ]
$\boldsymbol{T_o}$	Substrate temperature	294	K

Pixel exposure time (setting) & resulting segment angle (Experimental, No DBEA) (Figure 12e)

$\boldsymbol{\tau_d\ (ms)}$	$\boldsymbol{\zeta}$
3.567	33.3

Table S11. DBEA Parameters for Figure 12f

Parameter	Definition	Values	Units (*)
f_a	Fraction of absorption path through deposit	0.62	[ ]
δ_I	SE(I) yield per PE	0.65	[ ]
Δs	Span of concentration gradient in the BIR	80	nm
P	Precursor pressure (@ BIR)	0.65	$mTorr$
T_o	Substrate temperature	294	K

Pixel exposure time (setting) & resulting segment angle (Experimental, DBEA) (Figure 12f)

$\tau_{d,o}$ (ms)	ζ
3.567	39.2

Table S12. Simulation parameters for Figures 13 (a–b, e–f)

Parameter	Definition	Values	Units (*)
E	Electron beam energy	30	keV
i_b	Electron beam current	35	pA
r_b	Electron beam (FWHM)	6.5	nm
PtC_x	Deposit composition (Pt nanoparticles in C matrix)	PtC_8	
Φ	Precursor impingement flux	1758	$/nm^2 s$
Ω	Molecular volume (deposit)	0.175	nm^3
s_d	Deposit surface density	3.20	$/nm^2$
k	Thermal conductivity	0.16	$W/m\,K$
P	Precursor pressure at the BIR	0.6	$mTorr$

Simulation Input in addition to the constants listed in Table 2

Pixel exposure time (setting) & resulting segment angle (Simulation, No DBEA) (Figure 13a)

τ_d (ms)	ζ
4.608	21.4
5.138	26.5
8.227	47.4
9.638	53.0
11.501	58.7
22.020	71.9

Table S13. DBEA Parameters for Figure 13b, f

Parameter	Definition	Values	Units (*)
f_a	Fraction of absorption path through deposit	0.65	[ ]
δ_I	SE(I) yield per PE	0.35	[ ]
Δs	Span of concentration gradient in the BIR	80	nm
P	Precursor pressure (@ BIR)	0.60	$mTorr$
T_o	Substrate temperature	294	K

Pixel exposure time (setting) & resulting segment angle (Simulation, DBEA) (Figure 13b)

$\tau_d\ (ms)$	ζ
4.608	23.6
5.138	30.0
8.227	50.0
9.638	54.9
11.501	59.9
22.020	72.9

Pixel exposure time (setting) & resulting segment angle (Simulation, No DBEA) (Figure 13e)

$\tau_d\ (ms)$	ζ
4.608	22.9

Pixel exposure time (setting) & resulting segment angle (Experimental, DBEA) (Figure 13f)

$\tau_d\ (ms)$	ζ
4.608	24.8

Table S14. Simulation parameters for Figure 14a

Parameter	Definition	Values	Units (*)
E	Electron beam energy	10	keV
i_b	Electron beam current	48	pA
r_b	Electron beam (FWHM)	7.2	nm
PtC_x	Deposit composition (Pt nanoparticles in C matrix)	$PtC_{6.32}$	
Φ	Precursor impingement flux	1758	$/nm^2 s$
Ω	Molecular volume (deposit)	0.141	nm^3
s_d	Deposit surface density	3.68	$/nm^2$
k	Thermal conductivity	0.20	$W/m\,K$
P	Precursor pressure at the BIR	0.60	$mTorr$

Simulation Input in addition to the constants listed in Table 2

Pixel exposure time (setting) & resulting segment angle (Simulation, No DBEA) (Figure 14a)

$\tau_d\ (ms)$	ζ
2.540	9.36
3.198	27.23
4.020	40.82
5.342	49.22
8.710	63.6
17.530	76.2

Table S15. DBEA Parameters for Figure 14b

Parameter	Definition	Values	Units (*)
f_a	Fraction of absorption path through deposit	see below	[ ]
δ_I	SE(I) yield per PE	0.65	[ ]
Δs	Span of concentration gradient in the BIR	80	nm
P	Precursor pressure (@ BIR)	0.60	$mTorr$
T_o	Substrate temperature	294	K

Pixel exposure time (setting) & resulting segment angle (Simulation, DBEA) (Figure 14b)

$\tau_d\ (ms)$	f_α	ζ
2.540	0.40	15.6
3.198	0.60	30.5
4.020	0.70	42.2
5.342	0.70	52.6
8.710	0.70	65.3
17.53	0.70	77.2

Table S16. Microscope Parameters for Figures 15–18 <E_{10},i_{37}>

Parameter	Definition	Values	Units (*)
E	Electron beam energy	10	keV
i_b	Electron beam current	37	pA
r_b	Electron beam size (full–width at half–maximum)	7.2	nm
Λ	Exposure pixel point pitch	1	nm
A_xB_y	Substrate composition	$SiO_2(5\ nm)/Si$	[ ]
T_o	Substrate temperature	294	K

Table S17. DBEA Parameters for Figure 15–18

Parameter	Definition	Values	Units (*)
f_a	Fraction of absorption path through deposit	0.60	[ ]
δ_I	SE(I) yield per PE	0.65	[ ]
Δs	Span of concentration gradient in the BIR	80	nm
P	Precursor pressure (@ BIR)	0.55	$mTorr$
T_o	Substrate temperature	294	K

Pixel exposure time (setting) & resulting segment angle (Simulation, DBEA)

$\tau_d\ (ms)$	ζ
2.260	14.1
2.520	17.8
2.735	20.4
3.081	27.5
3.908	35.0
4.927	45.6
8.429	57.3
11.943	64.7

Supporting Information 2: details on segment angle calibration

An example calibration file required for DBEA usage. The file name is also provided that was used in the 3BiD software to create the exposure files and deposition experiments shown in Figures 15–18.

Table S18. Basic calibration file (Uncorrected). Electron beam pixel dwell time vs Segment angle (Modern_II_10keV.txt)

$\tau_d\ (ms)$	$\zeta\ (deg)$
1.750	0
2.000	5.2
2.250	9.8
2.500	14.5
2.917	24.2
3.248	25.8
3.718	33.6
4.370	38.4
15.379	69.8
28.314	77.1
52.915	80.9

Table S19. DBEA calibration files (DBEA Correction). Segment angle vs Segment thickness (Modern_II_10keV_angle_thickness.txt)

$\zeta\ (deg)$	$t_\zeta(nm)$
0	17.3
5.2	35.6
9.8	42.6
14.5	50.1
24.2	54.6
25.8	57.3
33.6	55.4
38.4	55.7
69.8	55.2
77.1	51.7
80.9	49.8

Table S20. DBEA calibration files (DBEA Correction). Segment angle vs Segment width (Modern_II_10keV_angle_width.txt)

$\zeta\ (deg)$	$w_\zeta(nm)$
0	10
5.2	21
9.8	23
14.5	25
24.2	26
25.8	28
33.6	29
38.4	30
69.8	37
77.1	38
80.9	41

Table S21. DBEA calibration files (DBEA Correction). Electron beam pixel dwell time vs Temperature @ segment origin* (Modern_II_10keV_tau_Tref.txt)

$\tau_{d,o}$ (ms)	T (K)
2.261	301.04
2.521	301.10
2.736	301.46
3.082	301.54
3.501	301.65
3.908	301.99
4.931	302.38
8.437	303.52
11.943	305.67
15.733	306.85

(*) At a glance, the relationship between electron beam dwell time at the segment origin and the reference temperature at the segment origin might imply, falsely, to the reader that dwell time directly influences thermal conditions in the deposit. It does not. In fact, the electron beam dwell time alone has no influence on thermal conditions, once steady–state thermal transport is achieved. Thermal transport is dictated only by the electron beam current and the pathlength of the primary electrons through the deposit. Why then, the reader might ask, does the reference temperature at the segment origin vary as a function of the initial electron beam dwell time? The answer is: *the electron beam dwell time pixel influences the cross–sectional area of the segment and therefore the thermal conductance of the segment*. Ultimately, the change in thermal conductance explains why the temperature changes. The segment cross–sectional area increases as a function of the initial segment dwell time[1]. This increases the absorption pathlength through the deposit and thereby the heating source term. This factor overwhelms the increase in conductance, due to the larger cross–sectional area, leading to an increase in the temperature at the BIR as a function of the initial electron beam dwell time for the segment.

Table S22. Process time vs Pillar height (Modern_II_10keV_time_height.txt)

t (s)	h (nm)
0	0
0.337	86.3
0.680	187.8
1.355	323.6
2.034	421.3
2.714	540.6
4.069	677.6
5.423	861.7

Supporting Information 3: statement on precursor coverage

In this paper, the techniques and methods used are restricted to (1) precursor physisorption at the surface and (2) precursor coverage is limited to a single monolayer of surface coverage at maximum coverage.

Supporting Information 4: explanations on reference frames

Three reference frames are of importance during 3D nanoprinting.

Reference Frame 1

The *global* reference frame has an origin at the substrate surface with the z–dimension is oriented normal to the substrate surface. The x– and y– coordinates lie parallel to the substrate plane.

$$(x, y, z) \quad [global]$$

This is the reference frame used during FEBID CAD definition using the 3BiD software program.

Reference Frame 2

A *local* reference frame is of interest when analyzing individual segment deposition ($\zeta < 90^o$), as part of a larger mesh object. This coordinate system lies at the origin of the segment–of–interest. The local system has only two coordinates

$$(x', z') \quad [local]$$

In this case, (x') is oriented along the projection of the segment in the electron beam focal plane. Thus, (x') is a function of both the x– and y– coordinates

$$x'(x, y)$$

(z') is related to (z) simply by a displacement to the origin of the segment–of–interest.

Reference Frame 3

Segment characterization and the development of the DBEA requires a pathlength based coordinate (s), which is naturally a function of x, y, and z, or

$$s(x, y, z)$$

The origin is defined based on the situation, e.g., it is useful to see the variation of FEBID relevant independent variables such (C) and (T) as a function of the s–coordinate along a particular segment in a mesh object model at some instant in time. In this case, the origin of the s–coordinate would be simply the segment origin. Further, the s–coordinate lies along the centerline of the nanowire/segment, paraxial to the wire. Importantly, measurements of segment angle for calibration purposes are made at s = 250 nm – this seemingly arbitrary selection is, in fact, by choice; at this position the segment is long enough to make a statistically meaningful angular measurements using SEM images while short enough such that deposition artifacts, ultimately leading to a segment bending, have not yet established.

Importantly, the s–coordinate is distinct from capital 'S'. Capital 'S' is used to reference to the current total length of a segment. Thus, S depends on time also.

$$S(x, y, z, t)$$

Therefore, 'S' can be used to refer to the segment growth rate and always describes the situation at the segment tip, i.e., the beam impact region (BIR).

Supporting Information 5: beam focus considerations

The depth of the field of the electron optical column is such that the beam focus changes negligibly, at the least over the scale of several micrometers above the substrate surface. However, if it is desired to deposit a mesh object model exceeding this rough limit then the impact of defocus on deposition must be accounted for.

Supporting Information 6: definition of SE_I

Secondary electrons generated by PE in the BIR are designed as SE_I.

Supporting Information 7: statement on calibration procedure

3D nanoprinting conditions are strongly dependent on the PE energy and current, beam size, precursor chemistry, local precursor pressure, substrate composition, the precursor–substrate interaction, and so on. Sensitivity to such a scope of variables requires the specification of these parameters for each calibration. Further, the gas injection system (GIS) used to deliver precursor to the BIR often requires mechanical alignments in preparation for 3D nanoprinting. This fact forfeits the possibility of returning *exactly* to any previous calibration recipe. Electron optical column alignments are also transient in nature. For these reasons, a calibration procedure must be routinely updated, even for the same conditions.

Supporting Information 8: considerations on nanoparticle metal-carbon matrix composite composition

De Teresa et al. studied the variation in composition of FEBID deposits as a function of primary electron beam energy[2]. Conveniently, the electron doses used during these studies are on the order of the typical primary electron dose used to deposit the pillar element during 3D nanoprinting, e.g., for a pillar on the order of nominally 500 nm, expressed in units of volume deposited per charge as demonstrated using the following calculation.

$$V_q' = \frac{\pi(35nm)^2 400\ nm \frac{\mu m}{1x10^9\ nm}}{\frac{48\ pC}{s}\frac{nC}{1000\ pC}1.7\ s} = 8x10^{-2}\frac{\mu m^3}{nC}$$

This example is derived from a nanopillar experiment conducted at 10 keV, 48 pA on the FEI Nova 600 using a 1.7s stationary beam dwell for pillar deposition. Compare this result with the values presented in Figure 2a of the De Teresa paper[2]. Further, De Teresa et al. report the composition of the deposit, in atomic percent carbon, as a function of primary electron beam energy. This data was extracted from the plot and a smooth function was applied to the data for use in the 3D nanoprinting simulation. The as–deposited nanostructure consists of small ~ 1–2 nm metal nanoparticles embedded in an approximately glassy carbon/amorphous carbon matrix. The

following function approximates the De Teresa nanoparticle composite composition variation with incident primary electron beam energy as

$$f_{Pt} = \frac{1}{1+8} + \left(\frac{1}{1+8} - \frac{1}{1+5}\right) e^{-\frac{E^2}{2(8keV)^2}}$$

where the purest composition in platinum occurs in the limit of relatively low primary electron beam energies with a composition of PtC_5 while the impure limit occurs at the maximum primary electron beam energy of 30 keV where the composition is PtC_8. (E) is used in the equation with the units of keV. Composition is defined by the parameter (f_{Pt}) which is the number of platinum metal atoms per total number of atoms in the deposit, i.e., the metal atomic fraction (at% Pt).

Supporting Information 9: justification for simulations

Simulations are a requirement due a current lack of viable experimental characterization methods at this spatial scale.

Supporting Information 10: definition of equilibrium precursor surface concentration

In the DBEA model, the equilibrium precursor surface concentration at the BIR edge is taken as simply the equilibrium concentration at the BIR, or

$$C_{eq}(S - \Delta s) \cong C_{eq}(S)$$

considering that the temperature change across the BIR Δs = 80 nm distance is negligible.

Supporting Information 11: explanation for temperature deviations from linearity

Notice that the temperature profile *along the pillar element* deviates from linearity. This occurs because the cross–sectional area of the pillar element varies along the s–coordinate. In this case, (q_b) is conserved via Fourier's Law through a balance between (dT/ds(s)) and (A(s));

$$\frac{dT}{ds}(s)A(s) = constant$$

Supporting Information 12: note about gap in TCN calculation

The gap need only be present during TCN calculation. The gap is absent in the actual CAD model that is converted into a stream file for real or simulated exposure.

Supporting Information 13: details on intermittent segment exposure

Consider the *continuous* deposition of a single segment. Digital scanning consists of a relatively long and stationary dwell time followed by an infinitesimal displacement (Λ = 1 nm) to the next pixel. This small displacement is nominally instantaneous. Now consider also, as already shown*, that the time required to reestablish steady–state heat transfer is approximately instantaneous, at least when compared with the magnitude of a typical pixel dwell time. Taken together, these facts suggest that a *quasi* steady–state condition persists during the transient heat transfer periods because the beam is barely displaced!

(*) see the Steady – State Heat Transport during 3D Nanoprinting section

Two additional factors that arise during 3D Comb exposure act to increase the fraction of total exposure time spent in the transient heat transfer period; (1) multiple beam exposures can be required to satisfy the total pixel dwell time and (2) multiple segments may be simultaneously deposited producing a beam sweeping motion that invalidates a *quasi* steady–state between adjacent pixel dwells. These factors combined potentially challenge the steady–state heat transfer approximation underpinning DBEA. Fortunately, the 3D Comb deposition using DBEA replicated 3D Comb CAD. For this reason, the increase in the deposition time under transient heat transfer must still be negligible. The following analysis of a specific electron beam exposure sequence during 3D Comb deposition reveals the presence of both factors in the CAD design.

Table S23. Sample of Electron Beam Shots during Intermittent Segment Exposure

$\boldsymbol{shot}$	$\boldsymbol{x\ (nm)}$	$\boldsymbol{y\ (nm)}$	$\boldsymbol{\tau_d\ (ms)}$	$\boldsymbol{pixel}$	$\boldsymbol{segment}$
441	0	100.61	4.032	n	2
442	0	100.61	4.032	n	2
443	0	100.61	4.032	n	2
444	0	100.61	4.032	n	2
445	-0.860	103.12	3.656	n+1	3
446	0.981	102.80	3.598	n+2	4
447	-0.860	103.12	3.656	n+1	3
448	1.961	102.99	3.598	n+3	4
449	-0.860	103.12	3.656	n+1	3
450	2.941	103.19	3.598	n+4	4
451	-1.719	103.62	3.656	n+5	3

Table S23 shows a sample of electron beam shots extracted from the 3D comb deposition. Shots 441–444 conclude the single segment element 2 on exposure level 2 while shots 445–451 begin the simultaneous exposure of segments 4 & 5 on exposure level 3.

The maximum intermittent exposure mode allows for simultaneous segment deposition. This introduces the concept of an exposure level. An exposure level may contain one, or multiple segments. The intermittent exposure sequence for the 3D Comb is provided Figure 16e; each segment is labelled according to the following key

$$Segment\ Index^{Exposure\ Level}$$

Table S23 provides partial list of 3D Comb exposure shots to demonstrate the ordering of exposure in maximum intermittent exposure mode.

Exposure level 3 is the first level that requires the deposition of multiple segments, specifically segments 3 and 4. It is instructive to examine exposure during the transition from exposure level 2 to 3. Table S23 provides details on 3D Comb exposure engaging deposition at beam shot 441. Shot 441 is the first of four shots required to expose the last pixel defining segment 2, listed as 441–444 in Table S23. This pixel has been arbitrarily assigned the index of (n) so that reader may understand the relationship between shots and pixels.

Often, multiple shots are required to exposure a single pixel because a maximum exposure time of 4.6 ms is imposed by a 12–bit DAC card currently used for patterning on the FEI Nova 600. When this limit is exceeded, pixels are fragmented into multiple shots of constant exposure time that (1) must sum to the pixel exposure time required and (2) yields an exposure time < 4.6 ms.

Advancing the analysis to exposure level 3, segment 3 contains the first pixel (n+1) to be exposed on level 3. $\zeta = 54.5^{o}$ for segment 3 which requires an initial dwell time per pixel of 10.968 ms per the calibration curve. This value exceeds the 4.6 ms limit and must be fragmented into shots. The fracturing procedure, described elsewhere[3], yields three shots, each of magnitude 3.656 ms. However, only a single shot is delivered (shot 445) before the beam shifts to segment 4 and pixel (n+2). Segment 4 has a smaller segment angle at $\zeta = 28^{o}$ and thus an exposure time of 3.598 ms. This value is below than the maximum exposure time limit and is thus completed in a single pixel exposure. The electron beam then returns to segment 3 to again expose pixel (n+1). In fact, a total of 3 pixels are exposed on segment 4 by the time that the first pixel on segment 3 is completely exposed.

Steady–state thermal conditions are invalidated anytime that the electron beam is displaced. Fortunately, once stationary, steady – state thermal conditions are quickly reestablished. However, the frequency of displacement increases (per unit length of segment deposited) when multiple shots are required per pixel.

REFERENCES

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