Molecular dynamics simulation of localized electrochemical deposition

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University of Cincinnati
Micro and Nano Manufacturing Laboratory
https://ceas.uc.edu/research/centers-labs/micro-and-nano-manufacturing-laboratory.html

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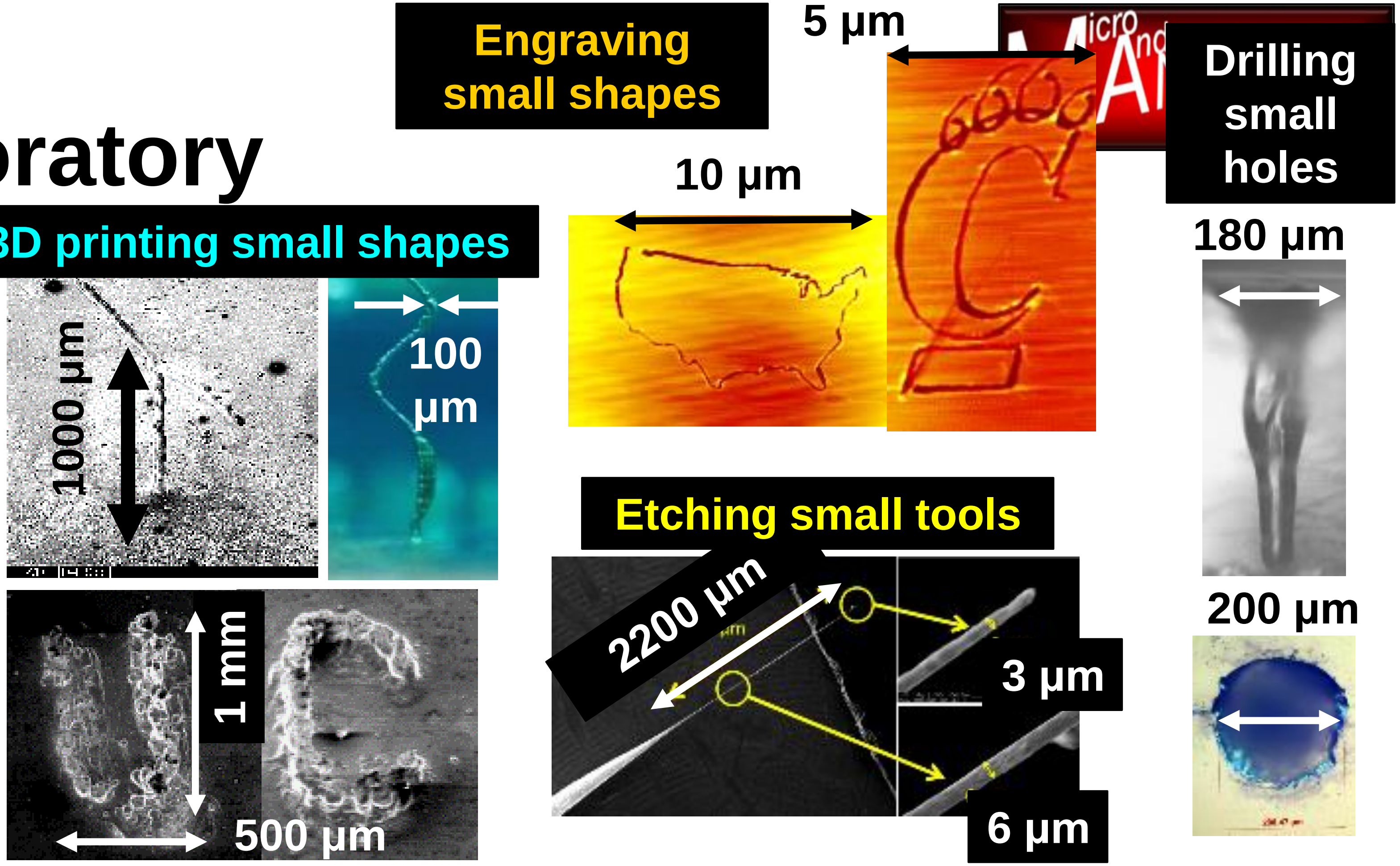
Outline

- **UC Micro and Nano Manufacturing Laboratory**
- Electrochemical Additive Manufacturing (ECAM)
- Why molecular dynamics?
- System setup and method
- Results and discussion
- Conclusions
- Acknowledgments

UC Micro and Nano Manufacturing Laboratory

- Technology grows increasingly smaller, lighter, and more powerful over time
- It has been possible by researching how to harness scientific principles to add or remove material at the small scale
- Our lab, the **Micro and Nano Manufacturing Laboratory**, performs this type of research to make a wide variety of micro and nano manufacturing processes possible, as seen in the images to the right



The long-term intention is for these technologies to eventually be commercially adopted.

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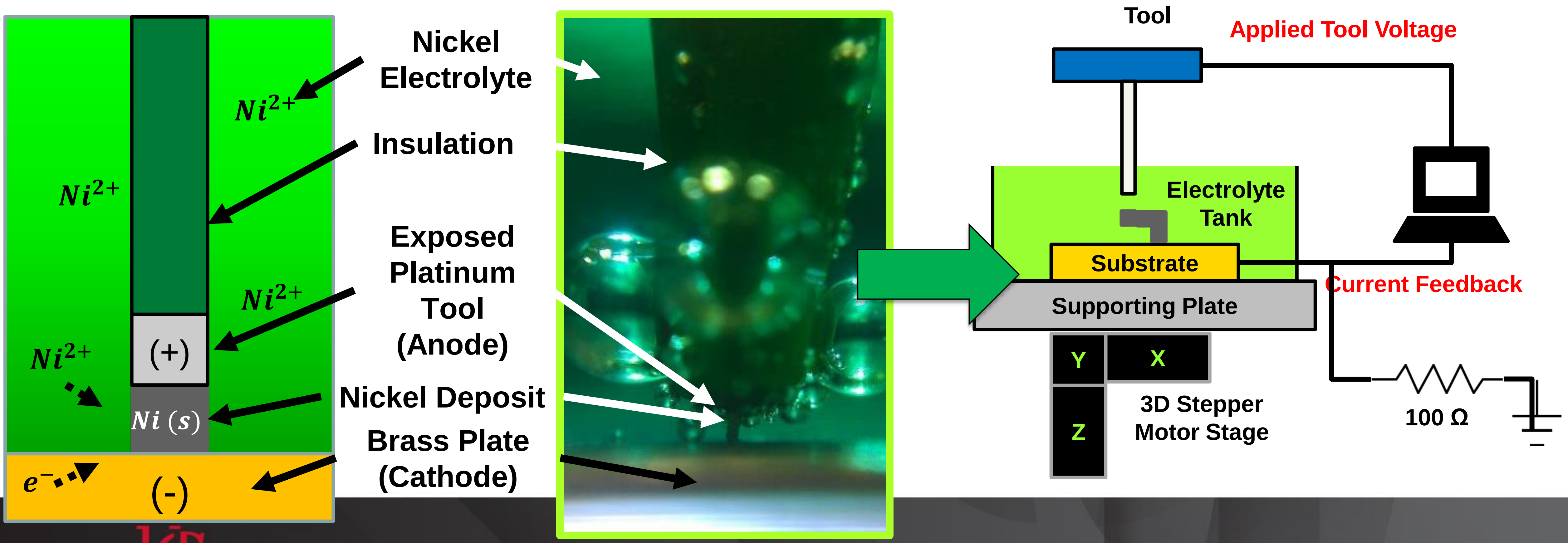
Electrochemical additive manufacturing

Introduction and working principle

- A nontraditional method of additive manufacturing
- Performed using localized metal deposition with 3-axis positioning and control



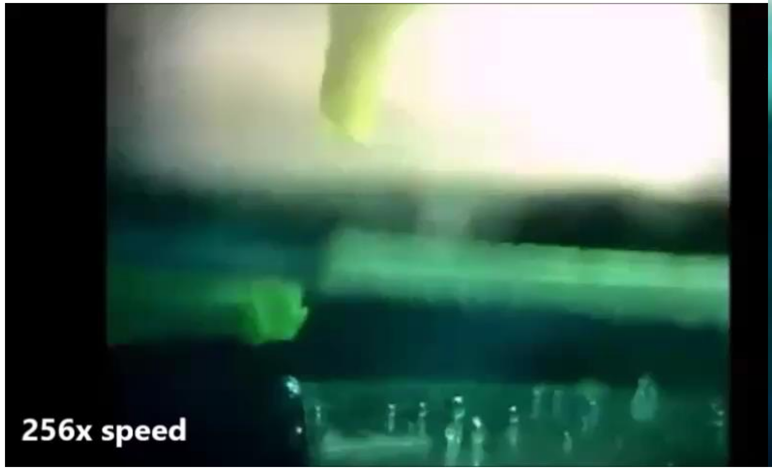
Feasibility study: Sundaram, Murali M., Abishek B. Kamaraj, and Varun S. Kumar. "Mask-less electrochemical additive manufacturing: a feasibility study." *Journal of Manufacturing Science and Engineering* 137.2 (2015).

Electrochemical additive manufacturing

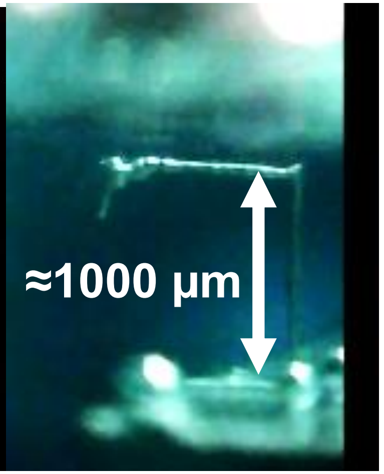
Video Demonstration: Overhanging Structure

- https://www.youtube.com/watch?v=0efMAGZI9XI
- This video shows the voxel-by-voxel nature of material addition by metal plating, which allows for support structures to be avoided

Video of Deposition



Resulting Shape



Advantages over conventional additive manufacturing methods

	MJ	ME	SLA	SLS	ECAM
Can deposit metal parts?	😐	☹	☹	☺	☺
Avoids support structures?	😐	☹	☹	😐	☺
Avoids residual stress/thermal defects?	😐	😐	☹	☹	☺
Avoids post-processing steps?	☹	😐	☹	☹	☺
Can achieve < 1 µm resolution?	☹	☹	☹	☹	☺

☺ = yes 😐 = somewhat ☹ = no

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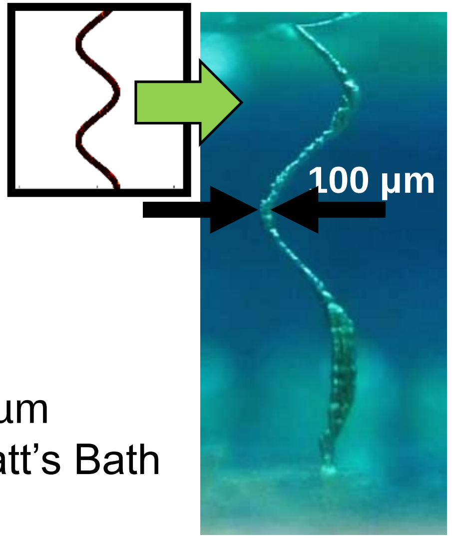
https://www.youtube.com/watch?v=0efMAGZI9XI

Electrochemical additive manufacturing

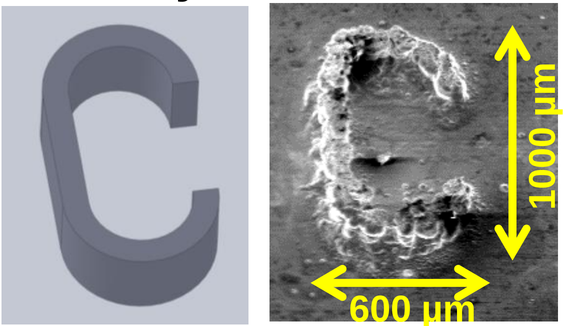
Experimental proof-of-concept

- A variety of CAD geometries can be created by ECAM, including support structure-less overhangs

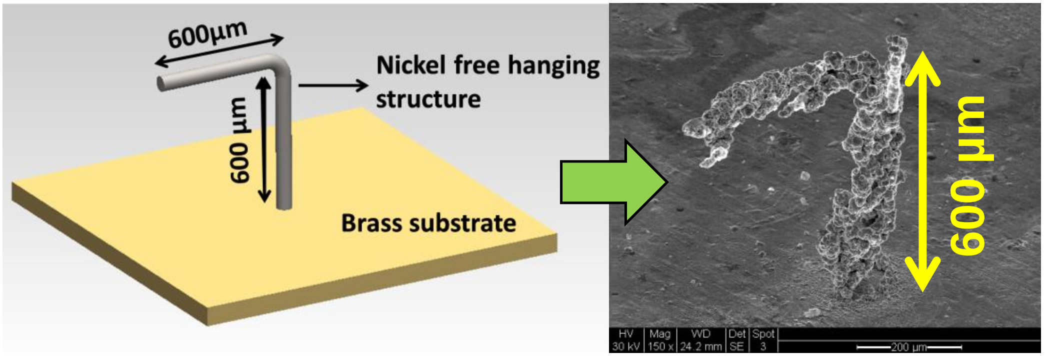
Helix Shape



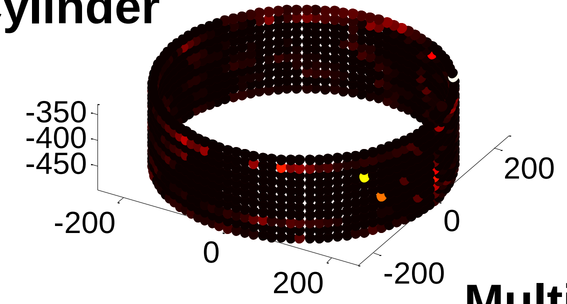
30-Layer Part



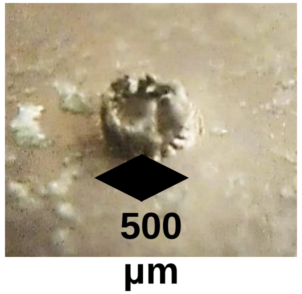
Overhang



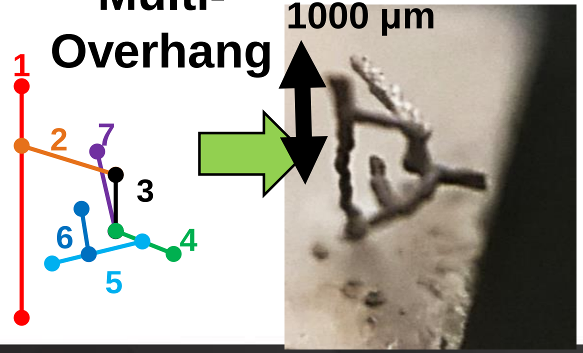
Cylinder



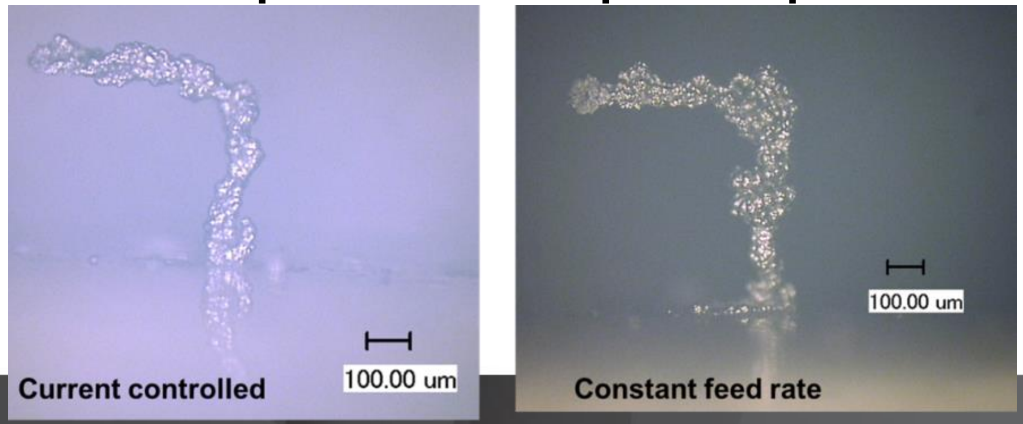
Tool size: 250 µm
Electrolyte: Watt's Bath
Voltage: 5 V



Multi-Overhang



Closed-Loop Control vs. Open Loop Control



Brant, Anne. *An Explorative Study of Electrochemical Additive Manufacturing*. MS Thesis. University of Cincinnati, 2016.

Sundaram, M., Kamaraj, A. B., and Kumar, V. S. (2015). Mask-less electrochemical additive manufacturing: a feasibility study. Journal of Manufacturing Science and Engineering, 137(2), 021006.

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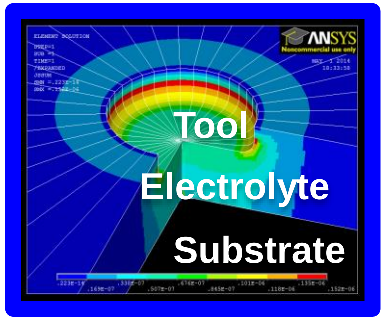
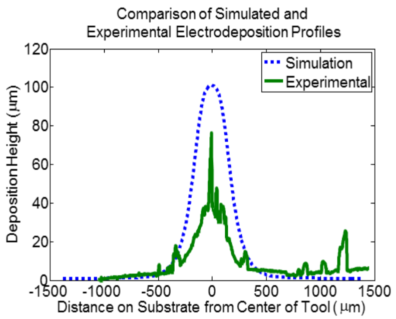
Electrochemical additive manufacturing

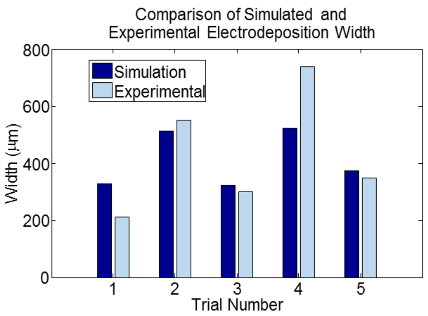
FEM simulations

MicroAndNanoMANUFACTURING Laboratory

Thermoelectric Simulation With Moving Boundary

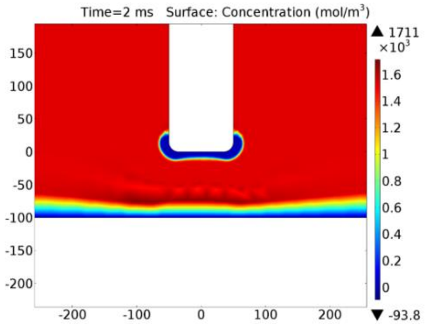


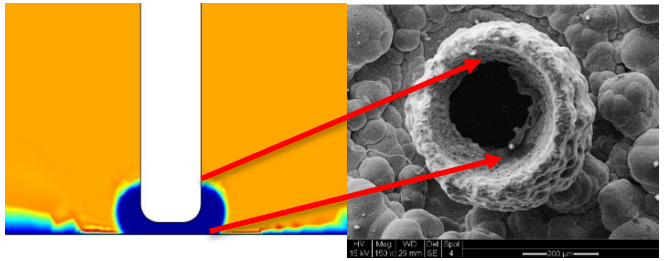




- Able to approximate deposition profile in response to varying input process parameters

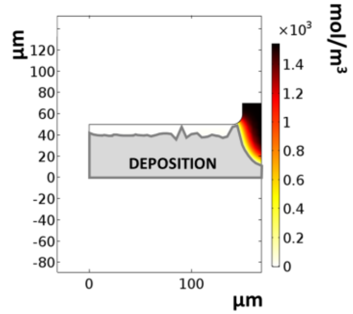
Concentration Change (Fick's Law) Simulation

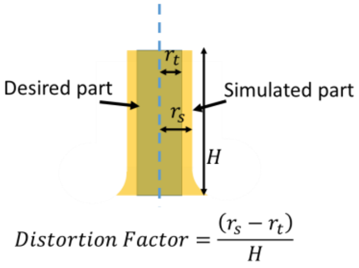


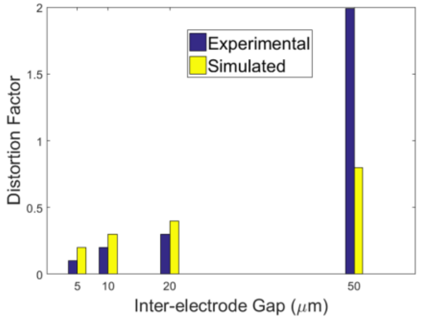


- Able to predict experimental ion depletion behavior at varying IEGs using the simulated concentration profile

Concentration Change With Moving Boundary







- Able to predict and minimize part distortion using results from changing process parameters in the simulation

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- Brant, Anne M., Murali M. Sundaram, and Abishek B. Kamaraj. "Finite element simulation of localized electrochemical deposition for maskless electrochemical additive manufacturing." *Journal of Manufacturing Science and Engineering* 137.1 (2015).
- Kamaraj, Abishek, Spenser Lewis, and Murali Sundaram. "Numerical study of localized electrochemical deposition for micro electrochemical additive manufacturing." *Procedia CIRP* 42 (2016): 788-792.
- Sundaram, Murali, Amy Drexelius, and Abishek B. Kamaraj. "A study on the effect of interelectrode gap in the electrochemical additive manufacturing process." *Machining Science and Technology* 23.2 (2019): 232-248.

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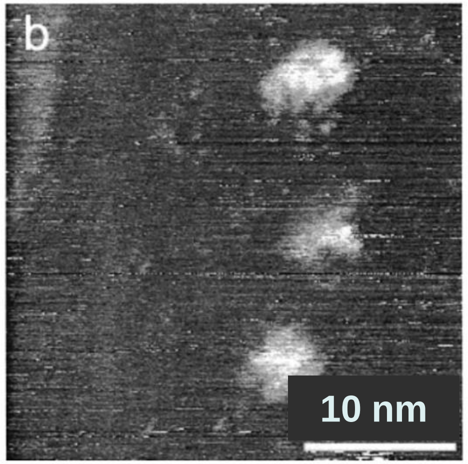
Why molecular dynamics?

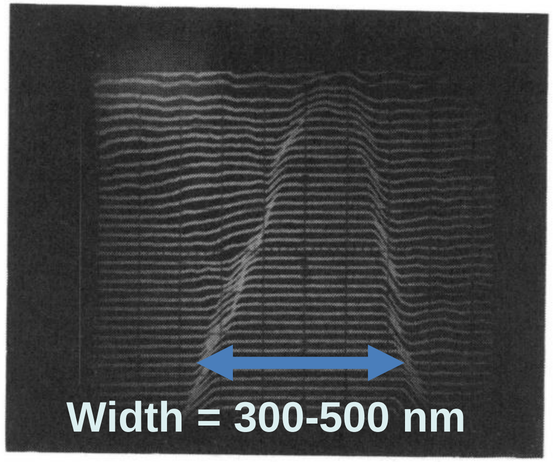
- ECAM is relatively unexplored at the nano scale
- Some work exists in using SPM probes (STM and AFM) to perform localized deposition

Cu Clusters on Au



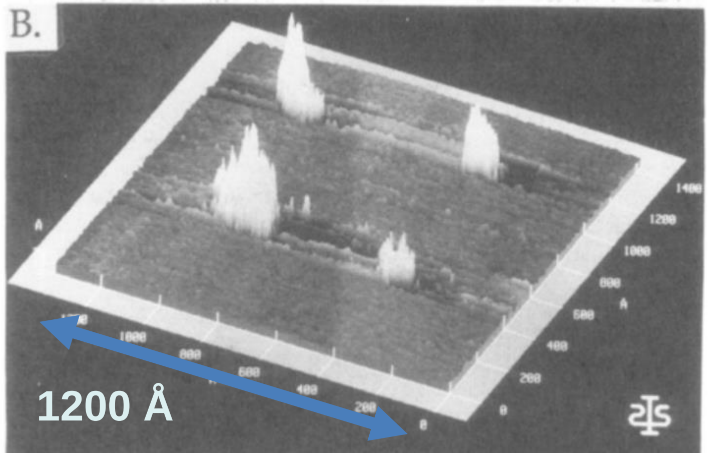
Kirchner, Viola, Xinghua Xia, and Rolf Schuster. "Electrochemical nanostructuring with ultrashort voltage pulses." *Accounts of Chemical Research* 34.5 (2001): 371-377.

Au Line on Au



Schneir, J., et al. "Creating and observing surface features with a scanning tunneling microscope." *1988 Los Angeles Symposium--OE/LASE'88*. International Society for Optics and Photonics, 1988.

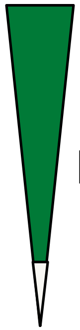
Cu and Ag Pillars on Graphite



Li, Wenjie, Jorma A. Virtanen, and Reginald M. Penner. "A nanometer-scale galvanic cell." *The Journal of Physical Chemistry* 96.16 (1992): 6529-6532.

Why molecular dynamics?

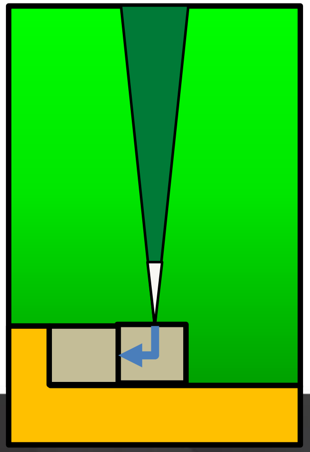
- Existing localized nano deposition work is limited in geometry to lines, pillars, and mounds
- Generally, SPM (scanning probe microscopy) techniques are used
- Challenges in deposition include:



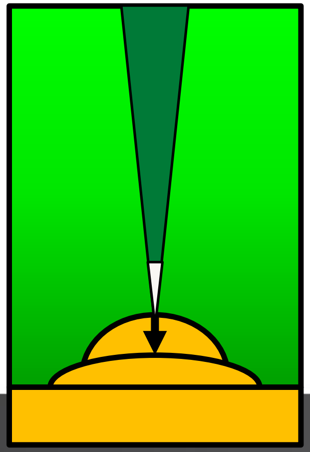
Scanning Tunneling Microscope (STM)

Atomic Force Microscope (AFM)

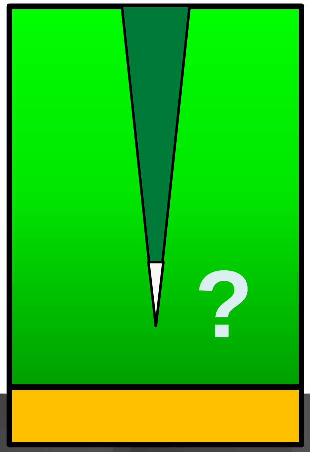
Lateral precision near surface defects



Surface diffusion after deposition

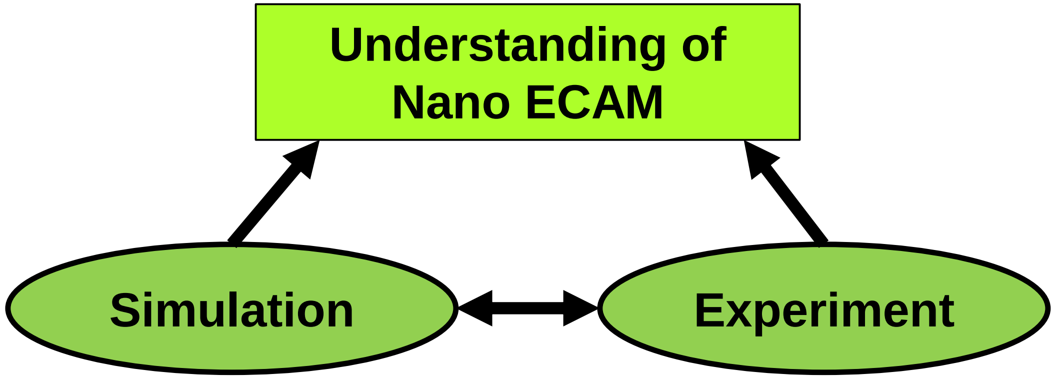


Low Repeatability



Why molecular dynamics?

- In order to achieve ECAM at the nano scale, we need:
  - The ability to deposit complex 3D shapes
  - The ability to reliably control where material is deposited and for it to stay in place
- This requires **a clear understanding** of the fundamental process of electrodeposition at the nano scale, achieved using:
  - Experiment
  - Simulation
- Use of molecular dynamics allows for the necessary atomic-scale resolution to model localized deposition at the nano scale



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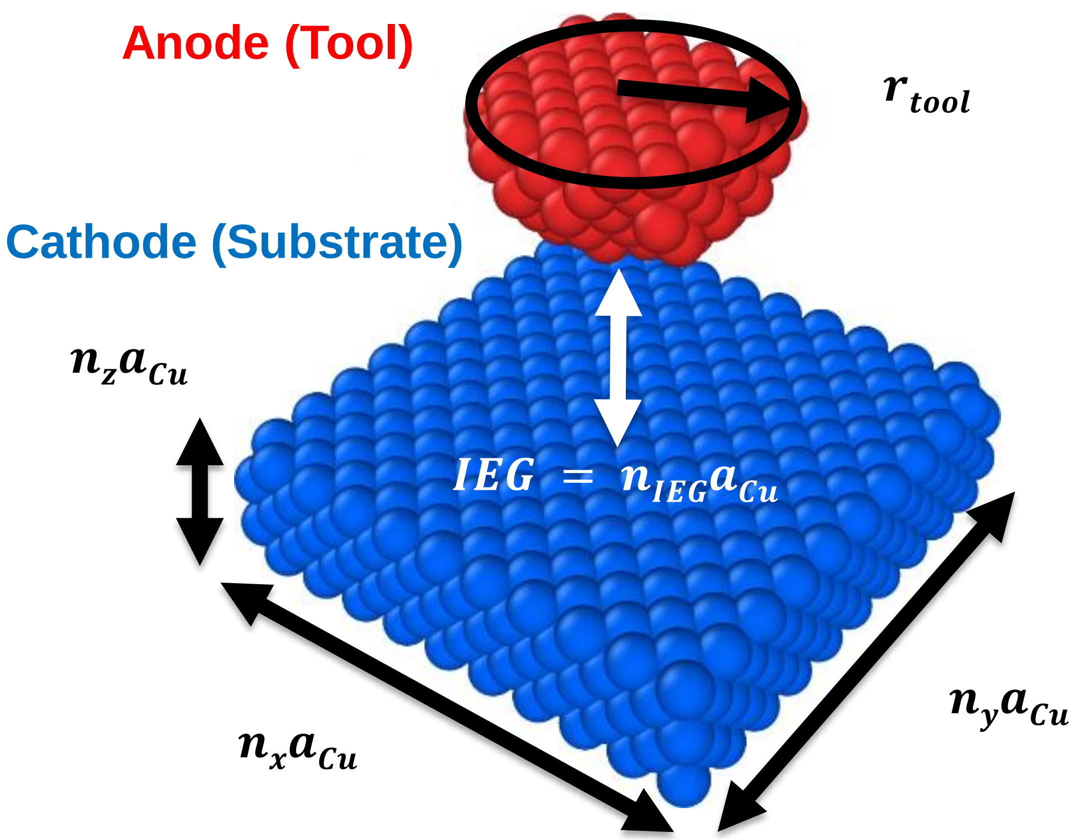
System setup and method

Electrodeconfiguration

- Anodic tool
  - Material: Platinum (Pt)
  - Hemisphere at top of the simulation region
  - Cut from a Pt FCC (100) lattice
  - Adjustable radius
- Cathodic substrate
  - Initially a flat FCC(100) copper slab (later, metal deposit grows on it)
  - Bottom of the simulation space.
- Interelectrode gap (IEG)
  - The space between and surrounding the electrodes where the electrolyte is contained
  - Lateral extent: borders of the cathode (side walls of the simulation region)
  - Vertical extent: cathode surface to the top of the anodic hemisphere (top wall of the simulation region)



System setup and method

Electrolyte species

- Explicit cations: Cu^{2+}
  - Metal cations, which are actively depositing
- Explicit anions: Cl^{-}
  - Act as a counter-charge
  - Some undergo specific adsorption to the substrate
- Solvent: implicit water via Brownian dynamics acting on the ions

Brownian dynamics equations (applied to each ion):

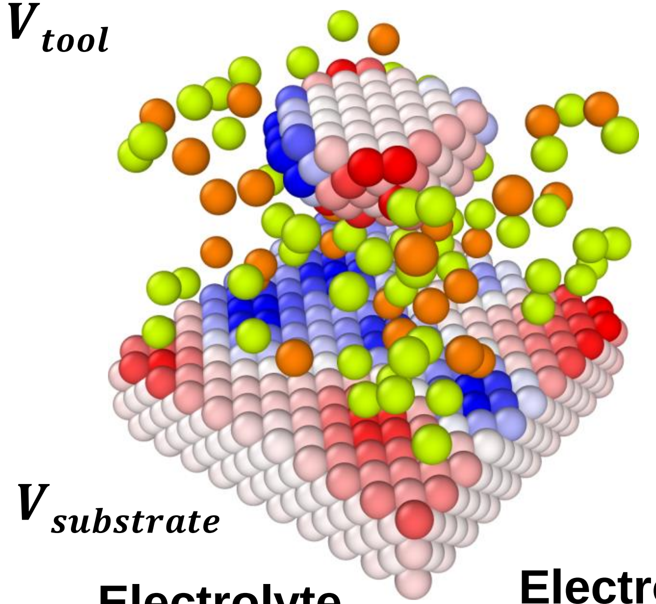
$$\boldsymbol{F_{net}} = \boldsymbol{F_{interaction}} + \boldsymbol{F_{frictional}} + \boldsymbol{F_{random}}$$

$$\boldsymbol{F_{frictional}} = -\xi_{\mathrm{fric}}\boldsymbol{v} = -6\pi \mathrm{r_i} \eta \boldsymbol{v}$$

$$\boldsymbol{F_{random}} = \left[F^{x}_{random}, F^{y}_{random}, F^{z}_{random}\right]$$

- $\boldsymbol{F_{net}}$ = net applied force
- $\boldsymbol{F_{interaction}}$ = interactions with surrounding ions and metal
- $\boldsymbol{F_{frictional}}$ = frictional force of implicit solvent
- $\boldsymbol{F_{random}}$ = random fluctuations of implicit solvent
- $\boldsymbol{v}$ = velocity of the ion
- $\mathrm{r_i}$ = ionic radius (of Cu^{2+} or Cl^{-})
- η = dynamic viscosity of implicit water solvent

Leach, Andrew R., and A. R. Leach. Molecular modelling: principles and applications. Pearson education, 2001.



Electrolyte
- Cu^{2+} Cation
- Cl^{-} Anion

Electrodes
- q >= .1
- q = 0
- q <= .1

System setup and method

Interatomic potentials

- Ion-ion and ion-electrode interactions
  - Coulomb interaction
  - Repulsive Lennard-Jones

$$U = \begin{cases} 4\varepsilon\left(\left(\frac{\sigma}{r}\right)^{12} - \left(\frac{\sigma}{r}\right)^{6}\right) + \varepsilon & if\ r \leq 2^{\frac{1}{6}}\sigma \\ 0 & if\ r > 2^{\frac{1}{6}}\sigma \end{cases}$$

  - Mixing rules:
  - $\sigma_{ij} = \sigma_{ii}\sigma_{jj}/2$ and $\varepsilon_{ij} = \sqrt{\varepsilon_{ii}\varepsilon_{jj}}$
- Copper substrate
  - Applied to copper substrate slab
  - The bottom layer of the slab was kept fixed for stability
  - Assumed to be not influenced by LJ or Coulomb interactions from the electrolyte
- Platinum tool
  - Inert: no Pt-Pt interaction + all atoms kept fixed

Potential Parameters

Ion	σ (Å)	ε $(kcal/mol)$	q
$Pt(s)$	2.845	7.80	varies
$Cu(s)$	2.616	4.72	varies
Cu^{2+}	2.616	4.72	2
Cl^{-}	4.40	.1	-1

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- Platinum and Copper: Heinz H, Vaia R, Farmer B, Naik R. Accurate simulation of surfaces and interfaces of face-centered cubic metals using 12− 6 and 9− 6 Lennard-Jones potentials. The Journal of Physical Chemistry C. 2008;112:17281-90.
- Chloride: Chandra A. Dynamical Behavior of Anion− Water and Water− Water Hydrogen Bonds in Aqueous Electrolyte Solutions: A Molecular Dynamics Study. The Journal of Physical Chemistry B. 2003;107:3899-906.
- EAM: Foiles S, Baskes M, Daw MS. Embedded-atom-method functions for the fcc metals Cu, Ag, Au, Ni, Pd, Pt, and their alloys. Physical review B. 1986;33:7983.

System setup and method

Electrode potentials

- Electrode voltages are held at constant voltages
- Constant-potential governing equation:

$$V_0 = \frac{q_i(t)}{\sqrt{\pi}\xi} + \sum_{a} \frac{q_a \,\mathrm{erf}\left(\frac{|\boldsymbol{r}_i - \boldsymbol{r}_a|}{\sqrt{2}\xi}\right)}{|\boldsymbol{r}_i - \boldsymbol{r}_a|} + \sum_{j \neq i} \frac{q_j \,\mathrm{erf}\left(\frac{|\boldsymbol{r}_i - \boldsymbol{r}_j|}{\xi}\right)}{|\boldsymbol{r}_i - \boldsymbol{r}_j|}$$

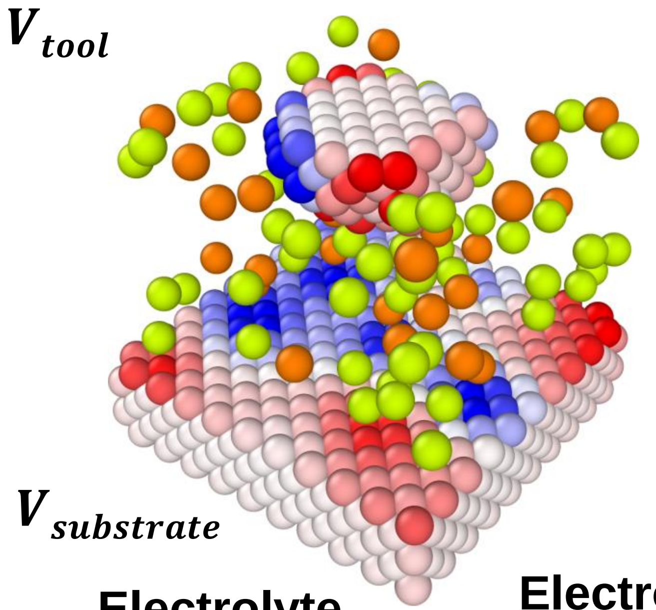
Siepmann, J. Ilja, and Michiel Sprik. "Influence of surface topology and electrostatic potential on water/electrode systems." *The Journal of chemical physics* 102.1 (1995): 511-524.

Where:

$V_0 = V_{tool}$ (for tool atoms)

or

$V_0 = V_{subs}$ (for substrate atoms)



Electrolyte

- Cu^{2+} Cation
- Cl^{-} Anion

Electrodes

- q >= .1
- q = 0
- q <= .1

System setup and method

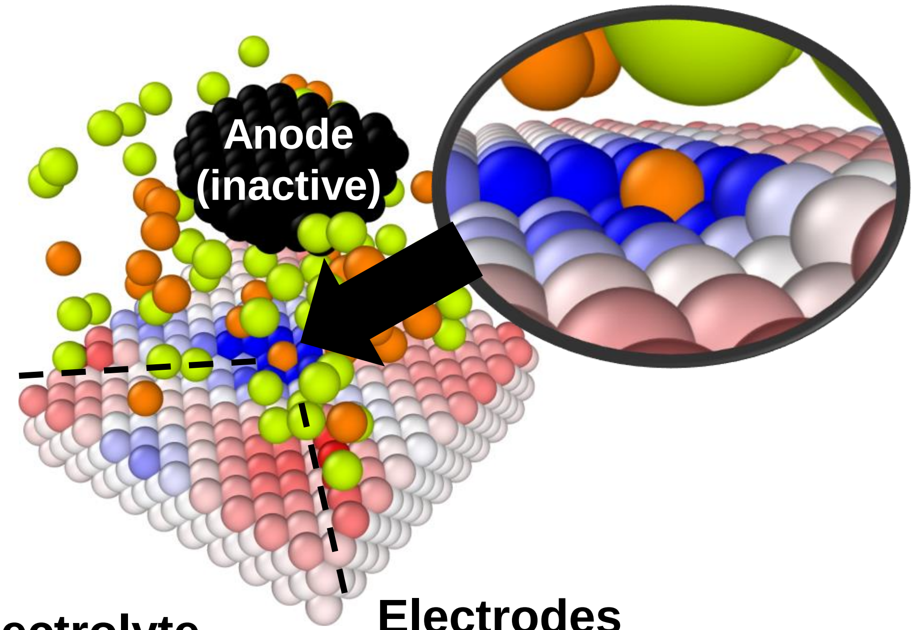
Potential reference for deposition

- A special simulation with an inactive tool and a cation in a substrate kink was run to compute a reference values $\boldsymbol{\mu}_0$ and $\boldsymbol{\varphi}_0^S$ for cation deposition
- This consisted of the sum of EAM and electrostatic interactions (respectively) for the cation in the reference kink position

Equilibrium Kink Condition

$$\boldsymbol{\mu}_0 = U_{EAM} \qquad \boldsymbol{\varphi}_0^S = \sum_{j \neq i} (kq_j/r_{ij})$$

Close-Up View



Electrolyte

- Cu^{2+} Cation
- Cl^- Anion
- Phantom Ion

Electrodes

- q >= .1
- q = 0
- q <= .1

Criterion for deposition reaction

- When the copper ion was near the substrate, two values were computed
- U_{EAM} = EAM potential if ion joins metal lattice in its current position
- $\boldsymbol{\mu} = \boldsymbol{\mu}_0 - ze_0(\boldsymbol{\varphi}_0^S - \varphi^S)$ = potential if ion remains aqueous
- If $U_{EAM} < \boldsymbol{\mu}$, then the ion was switched form the aqueous state to the metal state in its current position

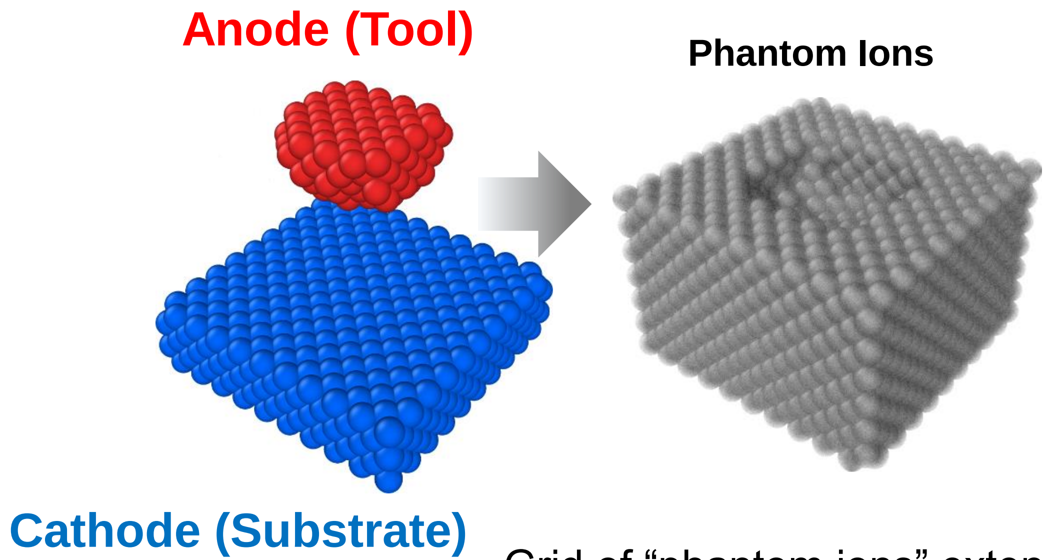
Idea based on:

- Simulation method using EAM vs fixed background potential: Mariscal, M., et al. "The structure of electrodeposits–a computer simulation study." *Applied Physics A* 87.3 (2007): 385-389.
- Role of overpotential in metal deposition: Paunovic, Milan, and Mordechay Schlesinger. *Fundamentals of electrochemical deposition*. Vol. 45. John Wiley & Sons, 2006.

System setup and method

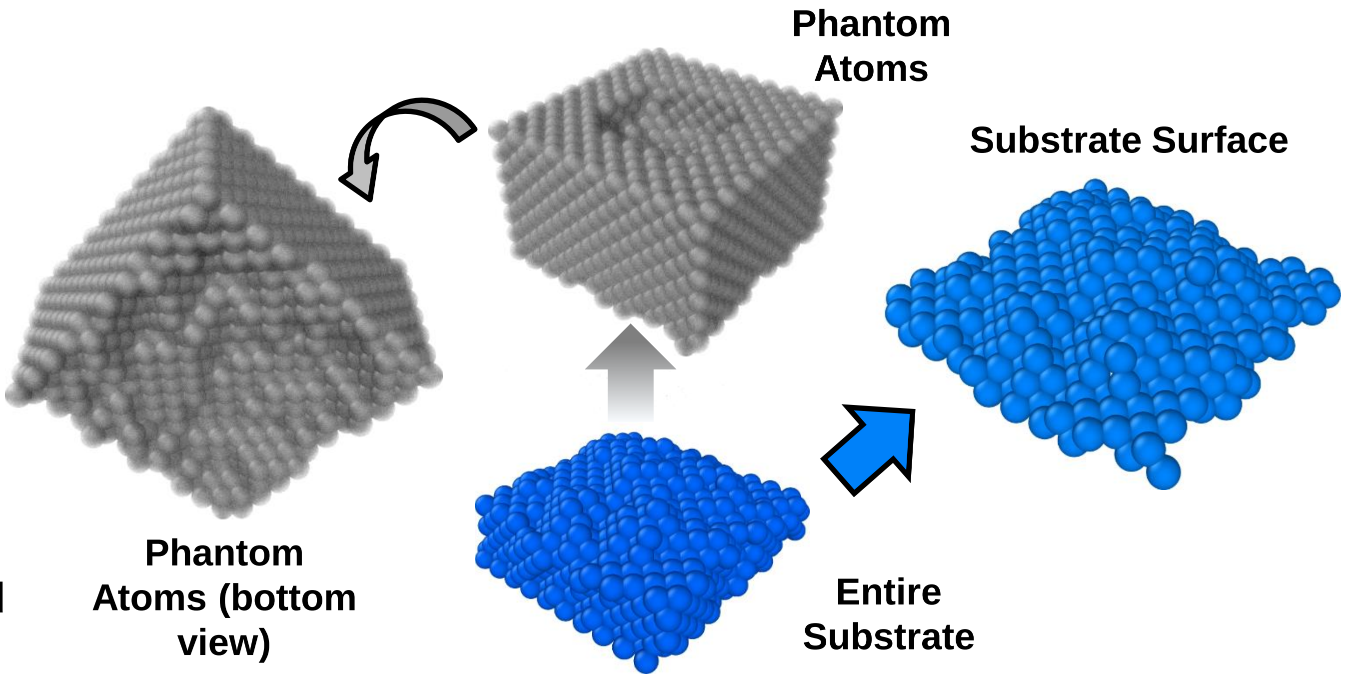
Phantom ion matrix

- A background grid of imaginary “phantom ions” (extension of Cu lattice) was used to assist with volume and surface area calculations



Grid of “phantom ions” extending from cathode lattice represents positions of atoms to be deposited

Growth of Deposit

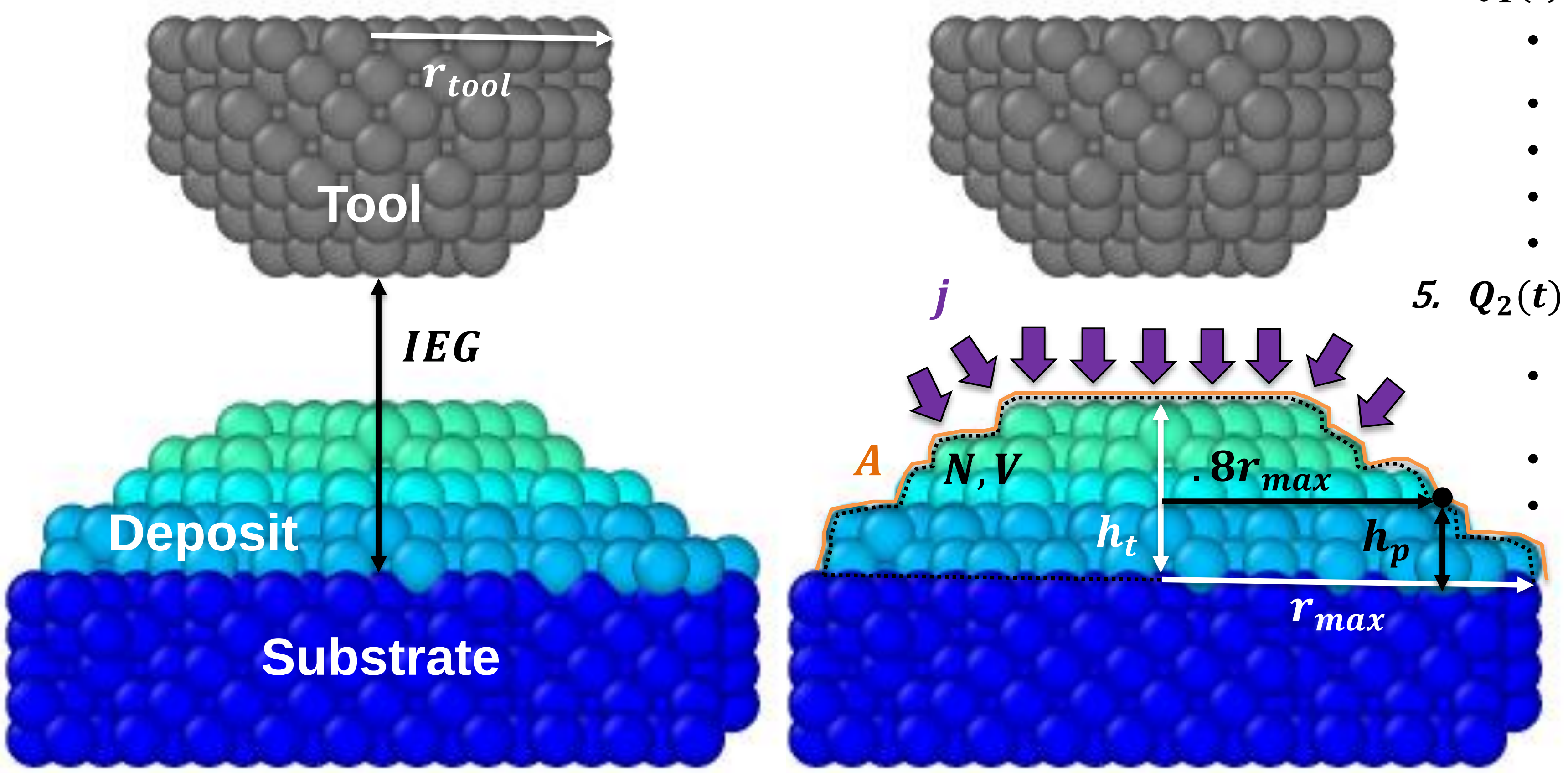


System setup and method

Postprocessing – evaluation of the deposition behavior

- Study effect of **input geometrical parameters** on **output deposit behavior**

1. Tool radius r_{tool}
2. Interelectrode gap IEG



1. $h_t(t)$ = Deposit height over time
2. $N(t)$ = Atoms deposited over time
3. $j(t)$ = Avg. current density over time
4. $Q_1(t)$ = Quality factor 1 (height ratio)
   - $Q_1(t) = \frac{h_t - h_p}{h_t}$
   - h_t = total height of deposit
   - r_{max} = max. radius of deposit
   - $.8r_{max}$ = 80% of r_{max}
   - h_p = plating height (height at $.8r_{max}$)
5. $Q_2(t)$ = Quality factor 2 (volume-area ratio)
   - $Q_2(t) = \frac{\left[\frac{V(t)}{A(t)}\right] - \left[\frac{V(0)}{A(0)}\right]}{\left[\frac{V(0)}{A(0)}\right]}$
   - $V(t)$ = volume of deposit
   - $A(t)$ = surface area of deposit

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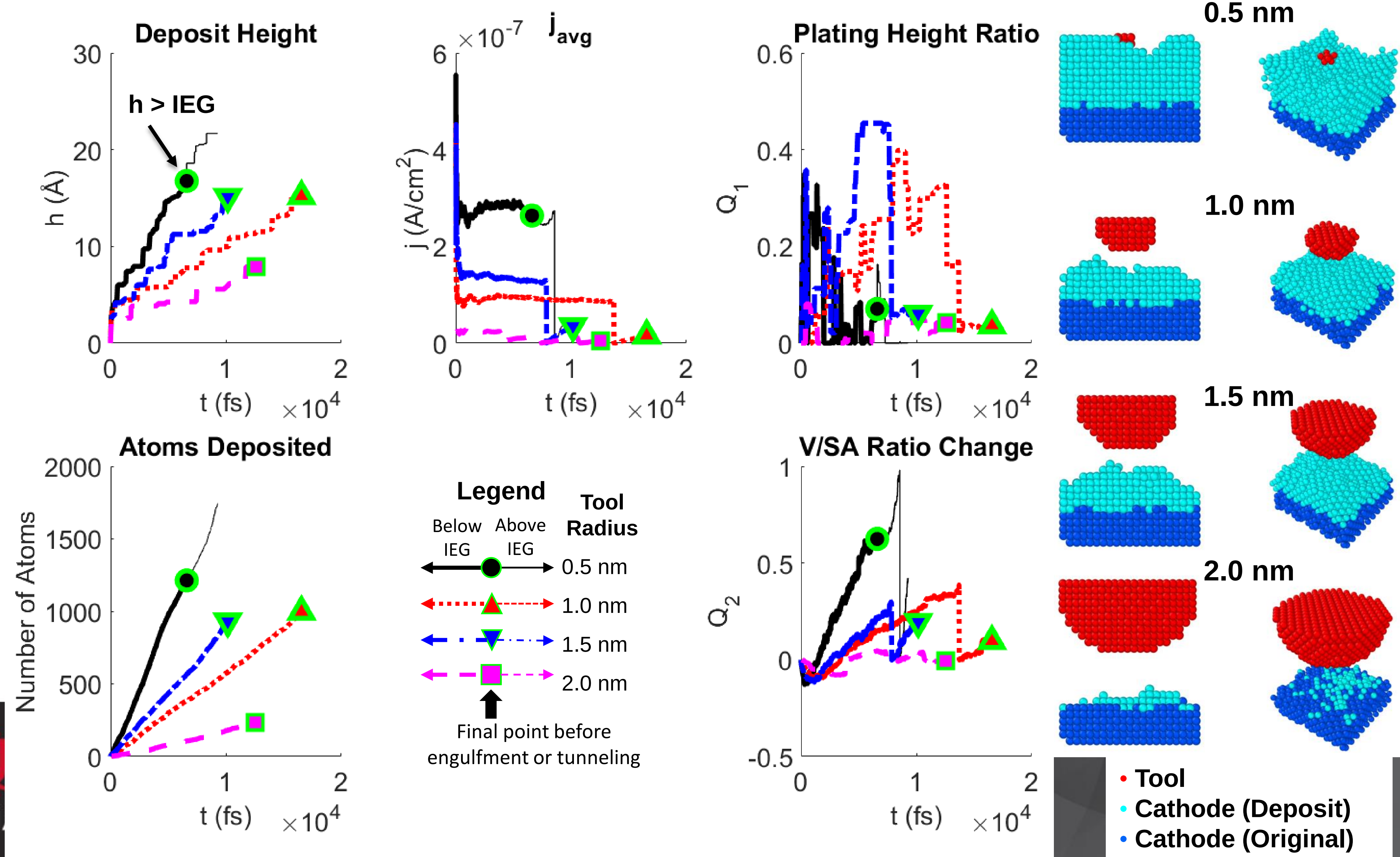
Results and Discussion

Effect of tool radius on the deposition behavior



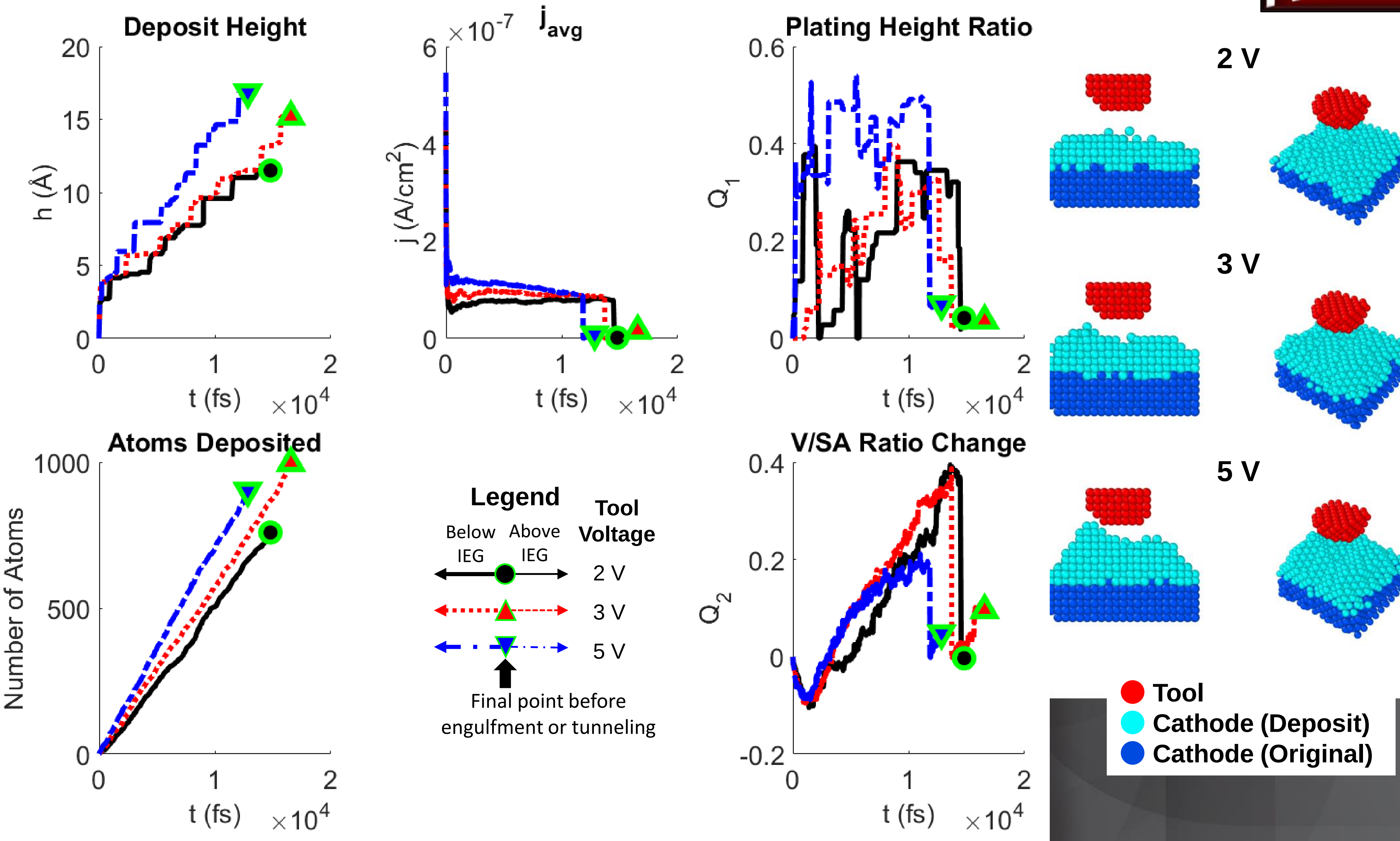
Results and Discussion

Effect of tool radius on the deposition behavior

- Effects of increasing the tool radius from intermediate values
  - decrease in deposit quality
  - likely due to distribution of the electric field and sparser charge density distribution
- Effects of reducing the tool radius from intermediate values
  - Also decrease in deposit quality
  - Likely explained by less atoms present to exert an electrostatic force on the cations
  - Even though the smallest tool would have had the strongest induced charges, electric field per atom, and overall current density
- Optimal radius
  - Under these conditions, an optimal radius value of 1.5 Å gives the best quality of deposition

Results and Discussion

Effect of tool voltage on the deposition behavior



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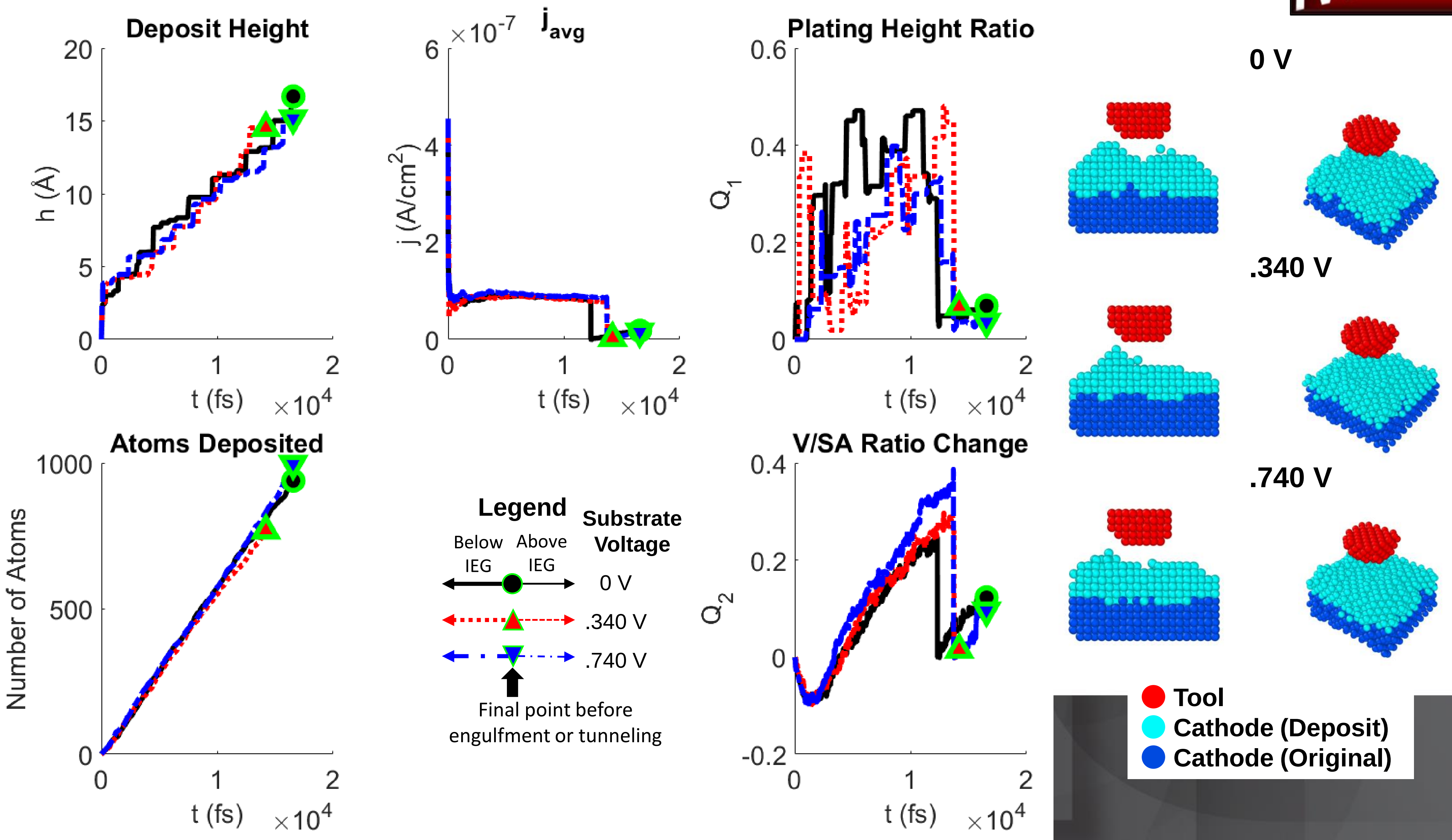
Results and Discussion

Effect of tool voltage on the deposition behavior

- Effects of increasing the tool voltage
  - faster deposition and ion depletion from electrolyte, leading to sharp initial drop in current density
  - Improved localization of the overall deposit, but hollow region in center of deposit due to ion depletion immediately beneath the tool
- Effects of reducing the tool voltage
  - Opposite effect

Results and Discussion

Effect of substrate voltage on the deposition behavior



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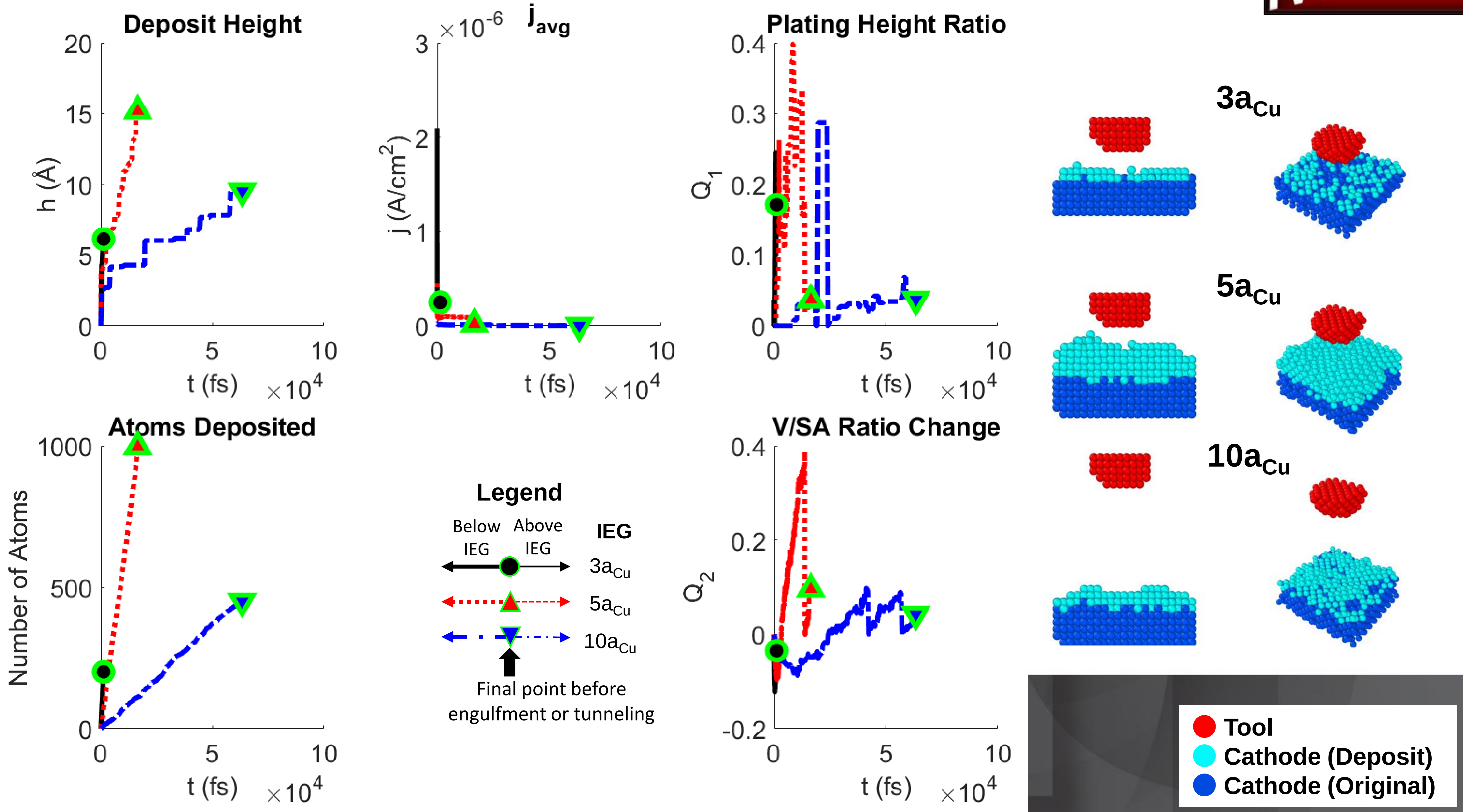
Results and Discussion

Effect of substrate voltage on the deposition behavior

- Effects of reducing the substrate voltage
  - Lowest value (corresponding to highest tool vs substrate difference) had similar effect as higher tool voltage - a faster ion depletion rate and hollow central region
- Effects of increasing the substrate voltage
  - Some subtle changes in the geometry and deposition rate, but not significant

Results and Discussion

Effect of interelectrode gap on the deposition behavior



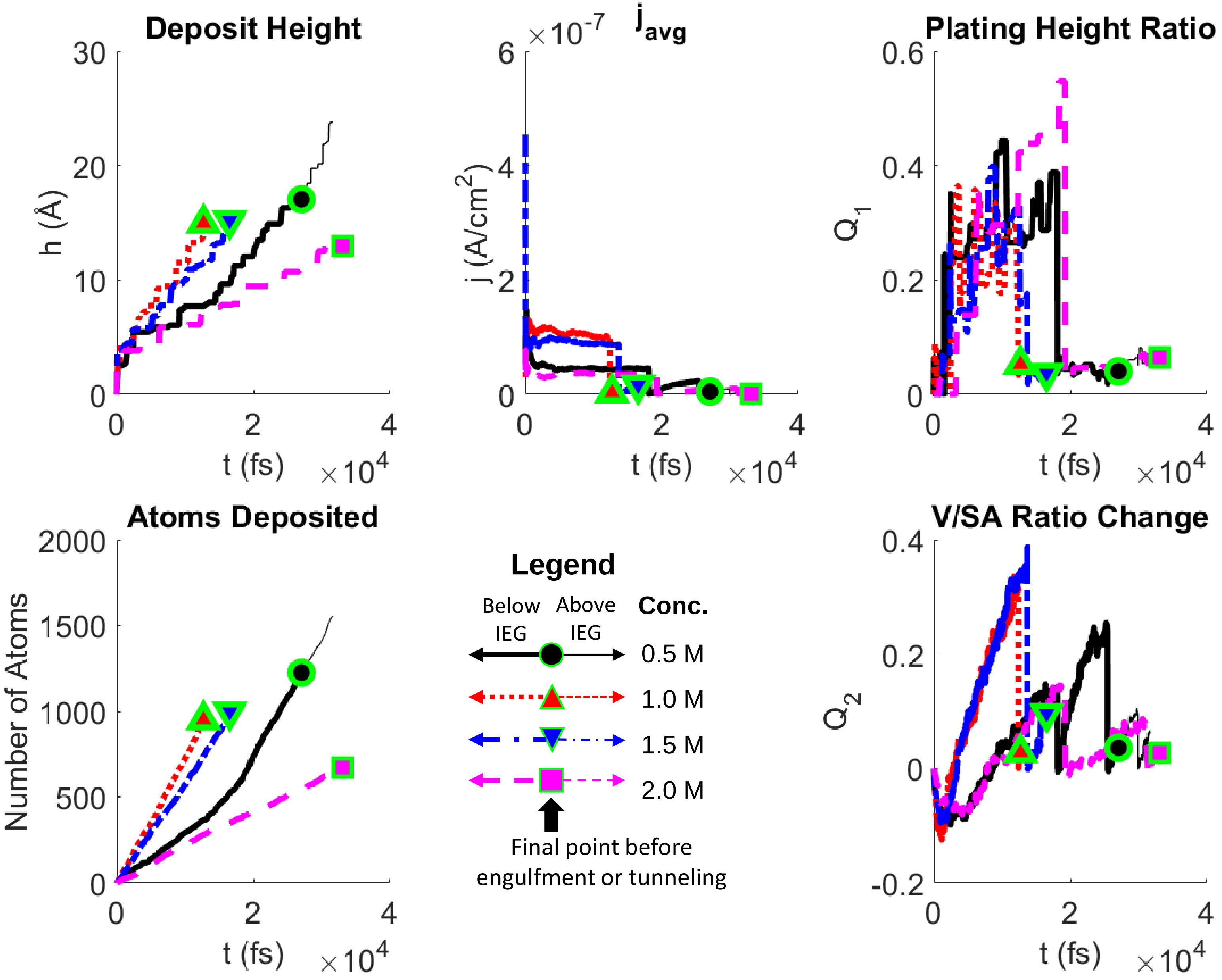
Results and Discussion

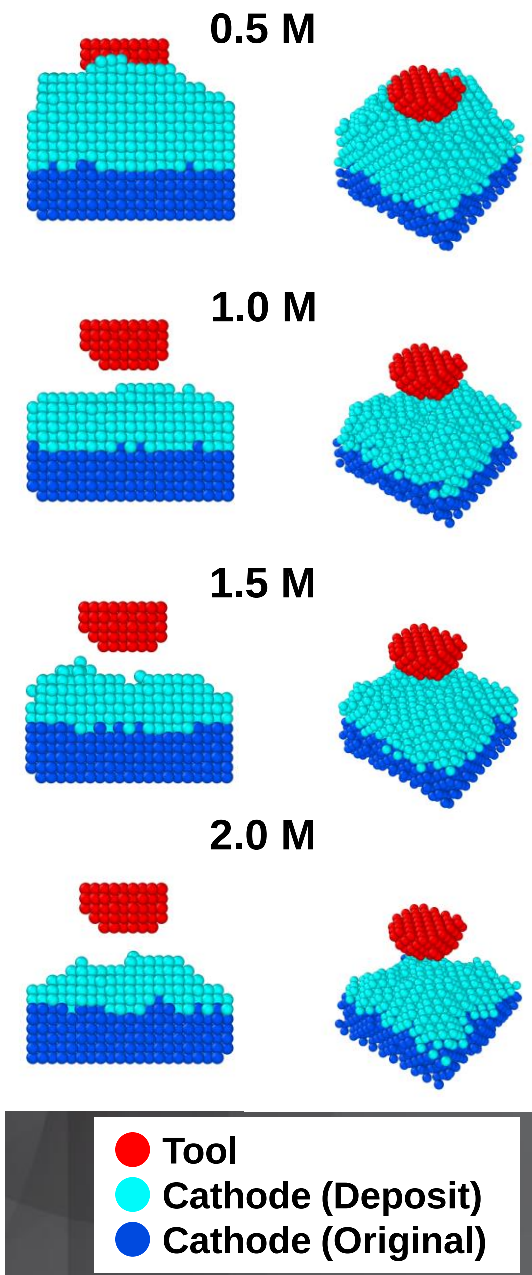
Effect of interelectrode gap on the deposition behavior

- Effects of increasing the interelectrode gap from the intermediate value
  - slower deposition
  - lower current density
  - Poor localization
- Effects of decreasing the interelectrode gap from the intermediate value
  - fastest deposition
  - rapid initial spike in current density
  - short-lived deposition resulting in a maximum height corresponding to two atomic layers
- Optimal interelectrode gap
  - The intermediate value of $5a_{Cu}$ yielded an optimally-localized deposit

Results and Discussion

Effect of ion concentration on the deposition behavior





Results and Discussion

Effect of ion concentration on the deposition behavior

- Effects of increasing the ion concentration from the intermediate value
  - lower deposition speed and current density
  - highest quality of localization
- Effects of decreasing the ion concentration from the intermediate value
  - also lower deposition speed and current density
  - lowest quality of localization
- Intermediate ion concentrations
  - Highest deposition speeds and current densities

Outline

- UC Micro and Nano Manufacturing Laboratory
- Electrochemical Additive Manufacturing (ECAM)
- Why molecular dynamics?
- System setup and method
- Results and discussion
- **Conclusions**
- Acknowledgments

Conclusions

Simulation method

- The localized electrochemical deposition process was modeled using a molecular dynamics simulation was performed
- Specifically, the migration and deposition of ions under the influence of charged, constant-potential electrodes was observed at varying input parameters (tool size, tool voltage, substrate voltage, interelectrode gap, and ion concentration)
- Deposition quality was evaluated quantitatively using two different quantitative approaches, as well as qualitative evaluation of the output geometry

Conclusions

Simulation output

- At a fixed interelectrode gap, the optimal radius for maximum deposition localization was found.
- Similarly, there was an optimal interelectrode gap at the radius studied for deposition quality,
- It was seen that varying the interelectrode gap and concentration allowed for inverse control over the deposition speed and quality – as deposition speed increased, quality decreased; and vice-versa.
- Variation of tool and substrate voltage gave a coupled change in deposition speed and quality, where both would simultaneously increase or decrease.
- Overall, with some exceptions, a higher tool-substrate voltage difference resulted in higher deposition speed and quality.
- Ion depletion behavior was seen in the runs with the highest voltage differentials and the lowest concentration, resulting in a hollow feature in the center of the deposit

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Thank you for your time!

Any questions?

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