Title: Polycrystalline On-Lattice Kinetic Monte Carlo Simulations of Electrodeposition

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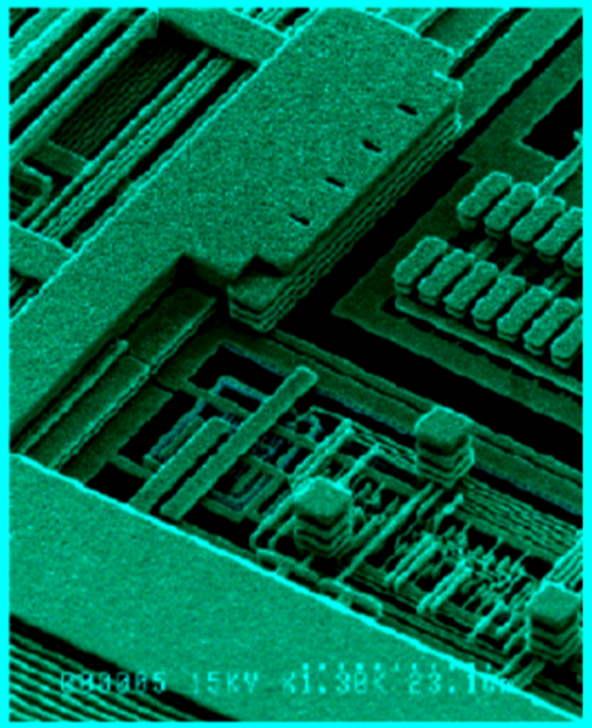
URL: http://pirsa.org/14050055

Abstract: The effects of the microstructure of metal films on device performance and longevity have become increasingly important with the recent advances in nanotechnology. Depending on the application of the metal films and interconnects certain microscopic structures and properties are preferred over others. A common method to produce these films and interconnects is through electrodeposition. As with every process the ability to control the end product requires a detailed understanding of the system and the effect of operating conditions on the resulting product. To address this problem a three-dimensional on-lattice kinetic Monte Carlo (KMC) method is developed to conduct atomistic simulations of polycrystalline metal electrodeposition. The method utilizes the highly descriptive embedded-atom method (EAM) potential to accurately describe the interatomic interaction energy. The EAM potential is a semi-empirical multi-body potential that accounts for the cohesive forces in a metallic system. Its parameters are determined from known experimental data.In the presented study kinetically controlled copper electrodeposition onto polycrystalline copper under potentiostatic conditions is modeled using the aforementioned KMC method. Two plating modes are considered: direct current and pulsed-plating. Three surface processes are considered during electrodeposition: deposition dissolution and surface diffusion. In addition to the surface processes diffusion along grain boundaries is also considered. The KMC method presented in this study is capable of simulating the copper electrodeposition process at the atomic level over long time scales on the order of seconds. The computational requirement of these serial KMC simulations are a fraction (hours versus days) of that required by the parallel molecular dynamics (MD) approach to simulate the same process over the much shorter time scales on the order of nanoseconds. Consequently this KMC method allows for the simulation of electrodeposition processes over time scales that are experimentally-relevant and not feasible using MD.

Introduction

- Certain microscopic structures and interfaces are desired in electrodeposition.
- There is a need to accurately predict operating conditions that will lead to these structures.
- Simulation-based research is an important approach to this problem.
  - Modeling both nanoscale crystal morphology and process dynamics.
  - Capturing the behavior in the bulk.



http://materials.usask.ca/photos/

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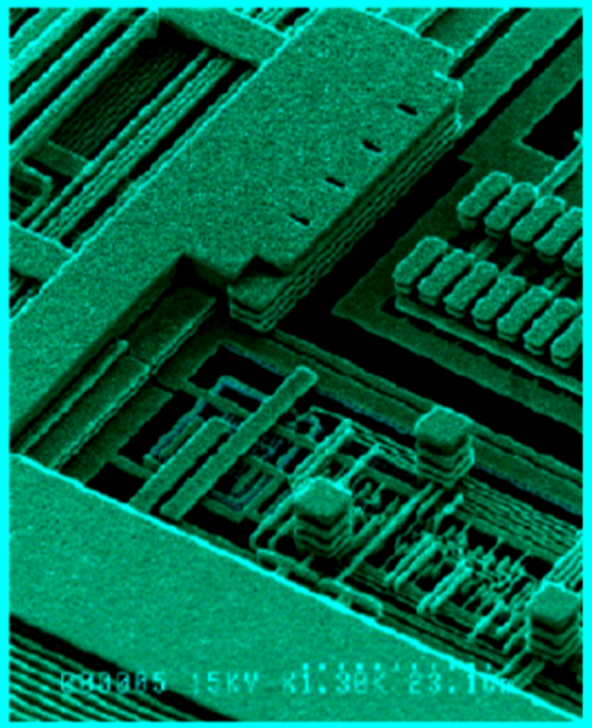

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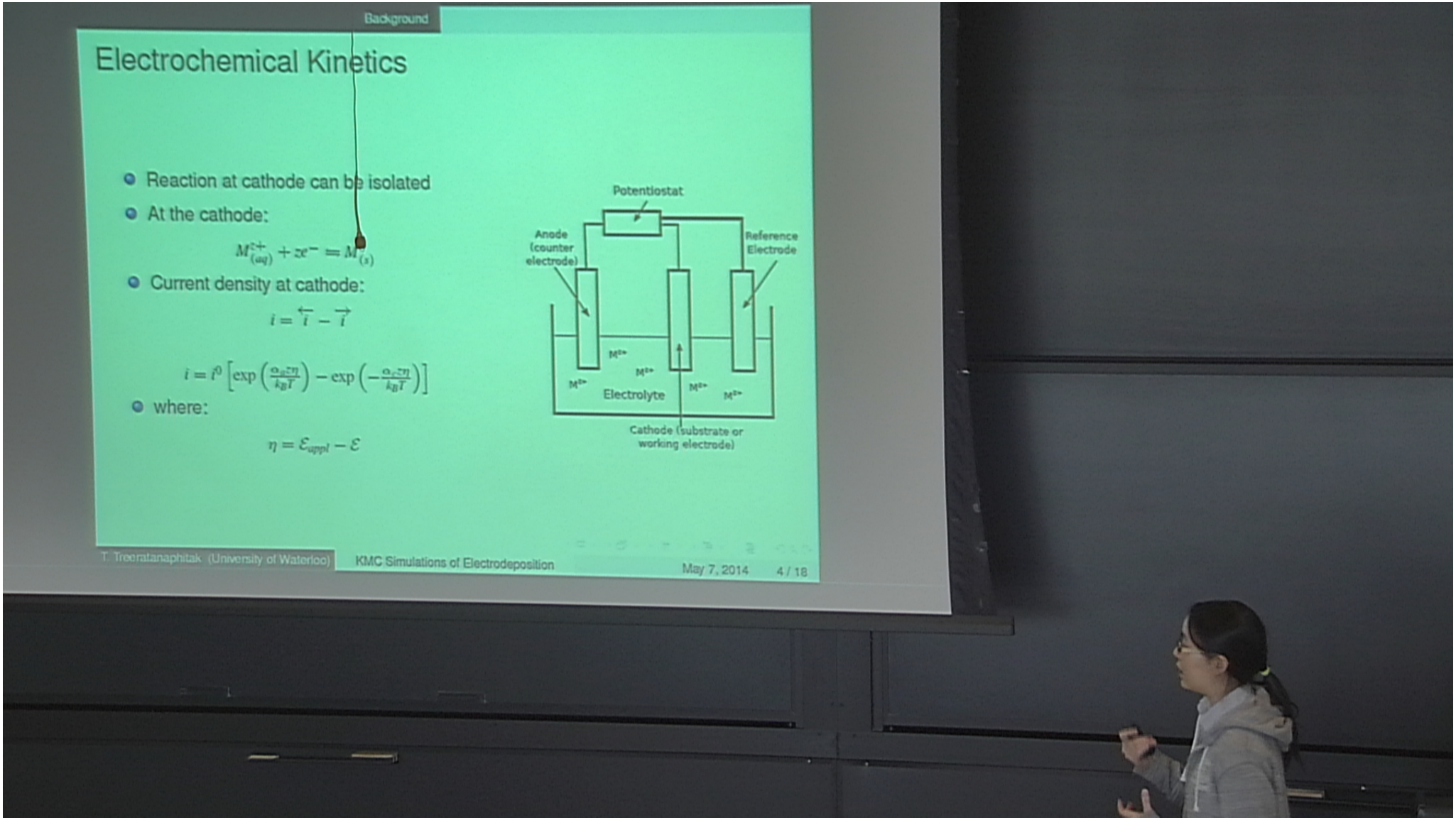
Background
Electrochemical Kinetics
Reaction at cathode can be isolated
At the cathode:
$M^{z+}_{(aq)} + ze^- \rightleftharpoons M_{(s)}$
Current density at cathode:
$i = \overleftarrow{i} - \overrightarrow{i}$
$i = i^0 \left[\exp\left(\frac{\alpha_c z\eta}{k_B T}\right) - \exp\left(-\frac{\alpha_a z\eta}{k_B T}\right)\right]$
where:
$\eta = \mathcal{E}_{appl} - \mathcal{E}$
Potentiostat
Anode (counter electrode)
Reference Electrode
Electrolyte
Cathode (substrate or working electrode)
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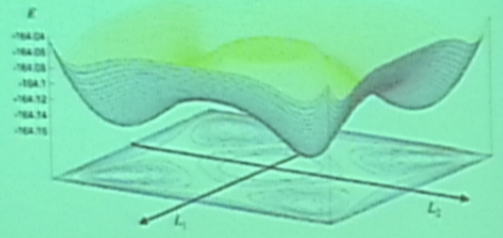
On-Lattice Kinetic Monte Carlo

- KMC involves coarse-graining in time and space (on-lattice approximation)
- On-lattice approximation – assumes that atoms vibrate about specific locations (minimum in potential energy)
- To move from one minimum to another – need to overcome energy barrier
- Location of metal atoms is restricted to sites on crystal lattice
- In KMC, the microscopic state of the system is only a function of position and time



(S. M. Woodley (2008) Chem. Phys. Lett.)

Embedded-Atom Method

- Semi-empirical multi-body potential based on quantum DFT calculations
- Parameters are obtained from fitting DFT calculations to known parameters of metal
- Embedding term (cohesive energy) + pair-wise repulsion term

$$E_i = F\left[\rho_i\right] + \frac{1}{2}\sum_{\substack{j \\ i \neq j}} \phi_{ij}(r_{ij}), \qquad \rho_i = \sum_{\substack{j \\ i \neq j}} \rho_h(r_{ij})$$

(M. S. Daw, M. I. Baskes (1984) Phys. Rev. B)

Methodology – Diffusion Mechanisms

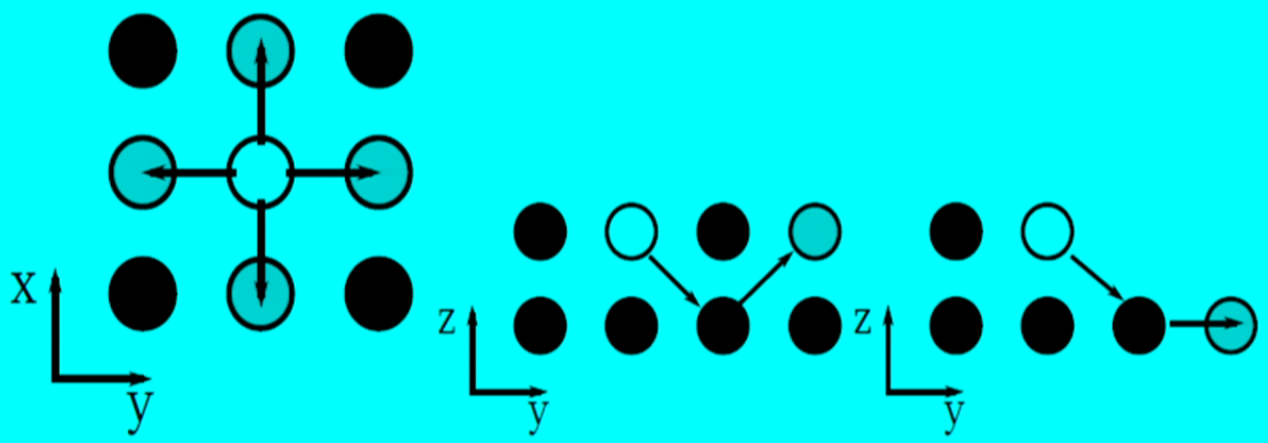


Figure: Schematics of three possible diffusion mechanisms: (left) hopping (middle) atom exchange and (right) step-edge atom exchange. White denotes an adatom, grey denotes the new location of the adatom, and black denotes an occupied site. *(T. Treeratanaphitak et al. (2014) Electrochim. Acta)*

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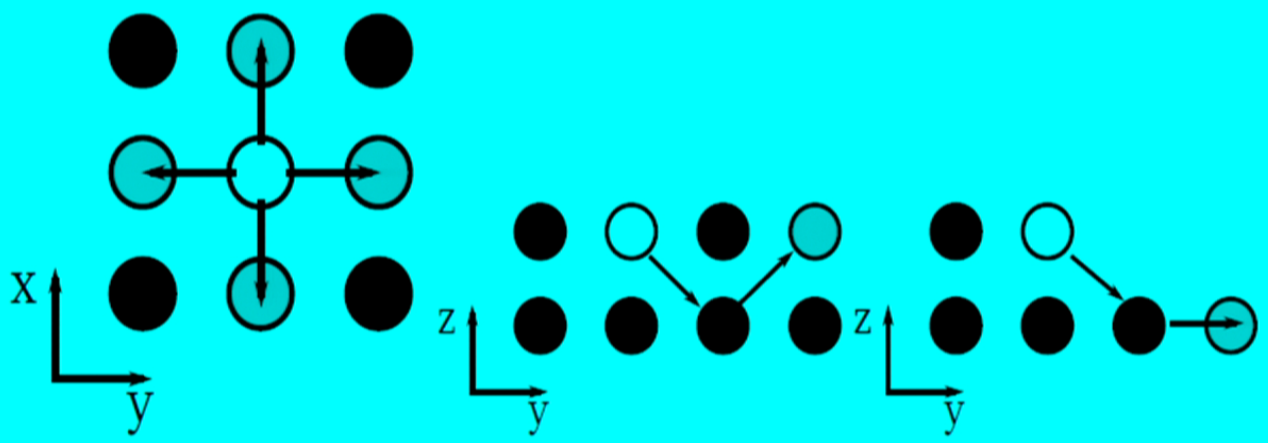

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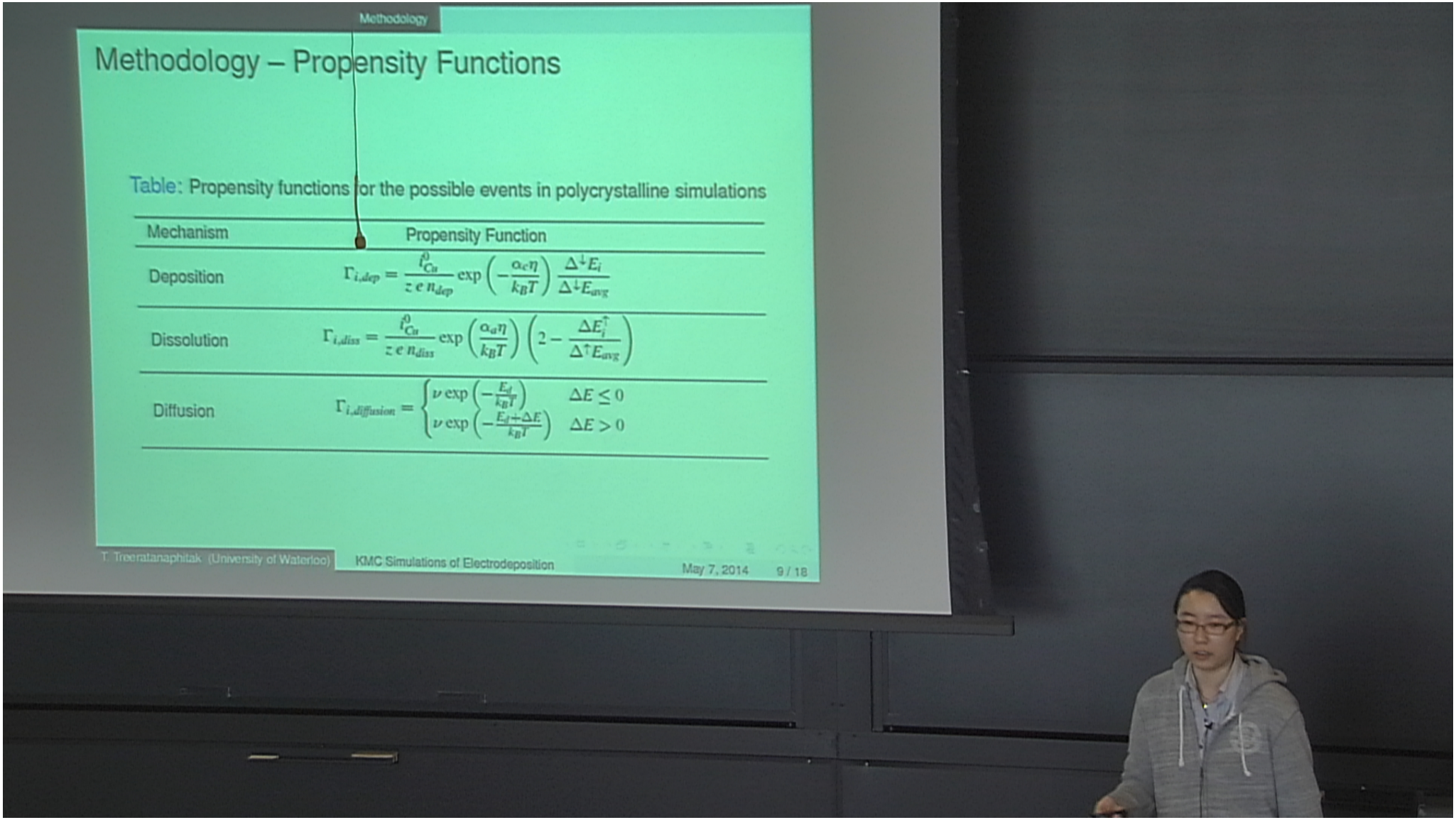
Methodology
Methodology – Propensity Functions
Table: Propensity functions for the possible events in polycrystalline simulations
Mechanism
Propensity Function
Deposition
$\Gamma_{i,dep} = \frac{i^0_{Cu}}{z\,e\,n_{dep}} \exp\left(-\frac{\alpha_c \eta}{k_B T}\right) \frac{\Delta^{\downarrow} E_i}{\Delta^{\downarrow} E_{avg}}$
Dissolution
$\Gamma_{i,diss} = \frac{i^0_{Cu}}{z\,e\,n_{diss}} \exp\left(\frac{\alpha_a \eta}{k_B T}\right) \left(2 - \frac{\Delta E_i^{\uparrow}}{\Delta^{\uparrow} E_{avg}}\right)$
Diffusion
$\Gamma_{i,diffusion} = \begin{cases} \nu \exp\left(-\frac{E_d}{k_B T}\right) & \Delta E \leq 0 \\ \nu \exp\left(-\frac{E_d + \Delta E}{k_B T}\right) & \Delta E > 0 \end{cases}$
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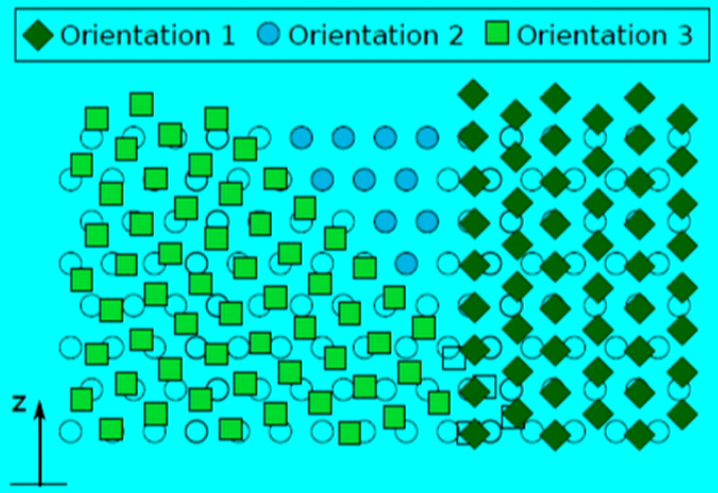
Methodology – Representation of a Polycrystalline System

- Coordinates of each grain are based on (100) reference coordinates

$$\mathbf{x}_i' = \mathbf{R}\mathbf{x}_i + \mathbf{T}$$

- Sites can overlap, but vacant sites will be inhibited



Results

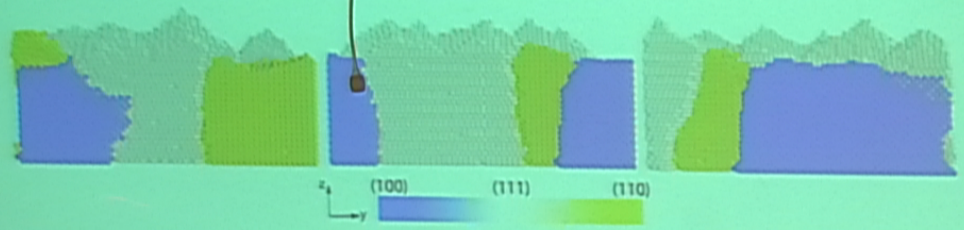
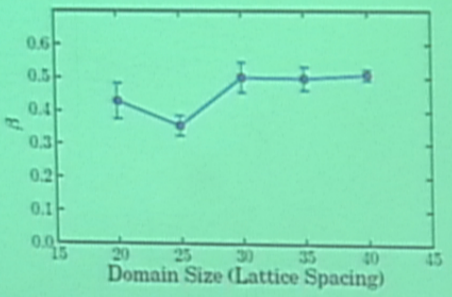


Figure: Side view of final deposit morphologies at (left to right) a) $\eta = -0.05$ V, b) $\eta = -0.10$ V and c) $\eta = -0.15$ V.

Results – Effect of Domain Size

- Finite size effect results in incorrect kinetics
- Need to identify minimum (critical) domain size
- Surface roughness-time power law relationship: $R_{RMS} = Ct^{\beta}$
- β converges to ≈ 0.5 after $30a \times 30a \times 40a$
- β is similar to β obtained experimentally



Results – Effect of Overpotential on Roughness

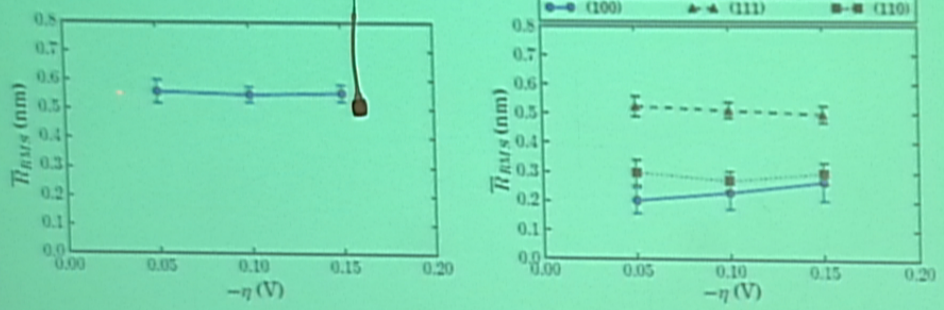
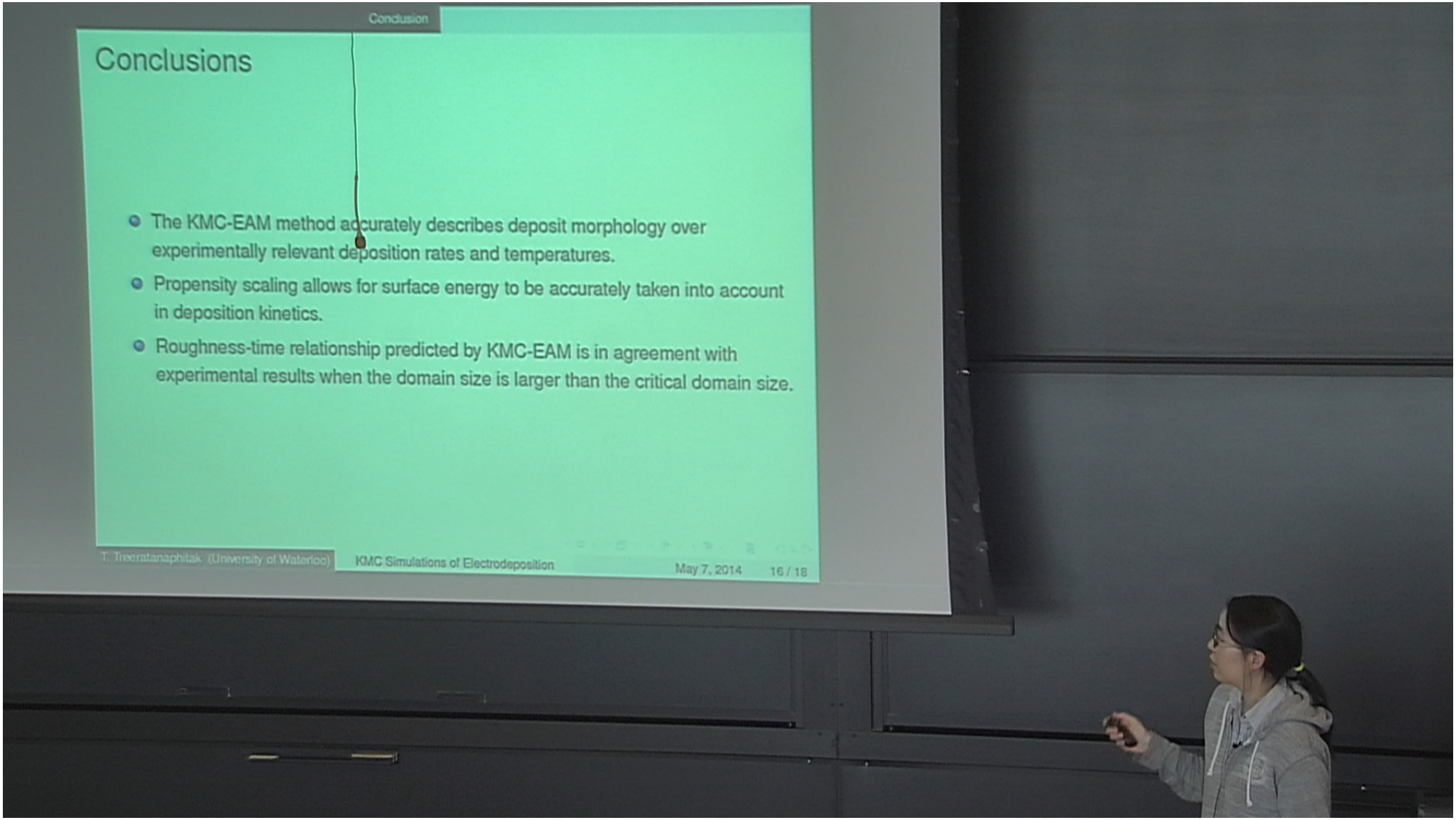


Figure: Variation of (left) the average final roughness and (right) the average final roughness of each grain orientation with overpotential.


Conclusion
Conclusions
The KMC-EAM method accurately describes deposit morphology over experimentally relevant deposition rates and temperatures.
Propensity scaling allows for surface energy to be accurately taken into account in deposition kinetics.
Roughness-time relationship predicted by KMC-EAM is in agreement with experimental results when the domain size is larger than the critical domain size.
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