# Atomic Scale Resolution for Stochastic Simulations of Electrodeposition at the Micrometer Scale

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Although Kinetic Monte Carlo (KMC) methods are widely used for simulating stochastic events during nucleation and deposit growth, their speed is seriously compromised when surface diffusion rates are rapid and KMC time steps are small. Such conditions arise, for example, under conditions of high ratios of surface-diffusivity-to-deposition-rate that result in widely spaced deposit clusters. While numerical coarse-graining and other approximate methods for speedup are available, it is, however, often also essential to retain accuracy at the atomic scale in order to simulate nucleation and early stages of deposit growth.

In this work we report on development of the "Exact Lattice First Passage Time" (ELFPT) algorithm, which allows for the accurate and efficient multi-scale numerical simulation of surface diffusion processes. We had previously shown [1] that ELFPT can improve the efficiency of sub-monolayer nucleation and growth simulations up to 100-fold over conventional KMC. However, those preliminary results were for a pristine physical system that was lacking in several important features required for the application to real-world electrodeposition systems.

In this presentation, we report recent results obtained with a next-generation ELFPT method that includes the following additional features: (1) treatment of edge diffusion in a First Passage (FP) fashion, (2) adaptation to additional lattice configurations beyond (100) to include the (111) family, (3) multi-layer growth for systems expressing Volmer-Weber and Stranski-Krastanov growth, (4) treatment of heteroepitaxial growth, with different reaction rates on substrate and deposit material, (5) consideration of defects (kinks, edges, voids), and (6) alloy systems.

The numerical simulations reported here seek to emulate some basic features of physical systems for which it may be feasible to compare with experimental data in the future. Numerical results will be presented for nucleation and growth of Ag onto inert, atomically smooth model surfaces under various deposition rates, metal ion concentrations, and temperatures. In addition, simulations of nucleation and growth in alloy systems are reported for the Ag-Au model system, where deposition occurs at low rates.

Mathematical analysis of the stochastic numerical data obtained for these systems has been carried out to obtain information that may be compared with experimental observations as, for example obtained by SEM or AFM. Such comparisons include time-dependent island-size and shape along with nearest-neighbor-distance and composition distributions.

Atomic-scale resolution is essential in certain nucleation systems for which the template for extended growth is defined at the atomic scale. The ELFPT approach has proven to be particularly efficient for situations of high ratios of surface-diffusivity-to-deposition-rate, which allow for the simulation of large domains in the range of a few micrometers without compromising the atomic-scale resolution. Such lengths scales are necessary in order to obtain statistically significant comparisons with experimental data such as obtained by SEM or AFM.

[1] A. Bezzola, B. Bales, R. Alkire, L. Petzold, "An Exact and Efficient First Passage Time Algorithm for Reaction-Diffusion Processes on a 2D-Lattice", submitted to J. Comput. Phys.