



# Kinetic Monte Carlo simulation of electrodeposition using the embedded-atom method



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## ABSTRACT

A kinetic Monte Carlo (KMC) method for deposition is presented and applied to the simulation of electrodeposition of a metal on a single crystal surface of the same metal under galvanostatic conditions. This method utilizes the multi-body embedded-atom method (EAM) potential to characterize the interactions of metal atoms and adatoms. The method accounts for collective surface diffusion processes, in addition to nearest-neighbor hopping, including atom exchange and step-edge atom exchange. Steady-state deposition configurations obtained using the KMC method are validated by comparison with the structures obtained through the use of molecular dynamics (MD) simulations to relax KMC constraints. The results of this work support the use of the proposed KMC method to simulate electrodeposition processes at length (microns) and time (seconds) scales that are not feasible using other methods.

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## 1. Introduction

The effects of microstructure of metal films on device performance and longevity have become increasingly important as recent advances in the reduction of interconnect dimensions progress. A specific example is the microstructure resulting from the copper damascene electroplating process [1]. Certain microscopic structures and interfaces between crystal grains in copper films have been found to improve the performance of interconnects [2,3]. For example, ‘bamboo’ grain structures and (111) orientation are preferred since they improve the lifetime of copper interconnects [3]. Thus, it is important to determine under which conditions the electrodeposition process yields these preferred structures.

A very effective method for simulation of the electrodeposition process, without resorting to first-principles calculations, is through the use of molecular dynamics (MD) that makes use of a suitable interaction potential. The embedded-atom method (EAM) potential has been shown to accurately characterize metal/metal interactions [4] and predict relevant dynamics for systems including hydrogen adsorption onto nickel and segregation in binary alloys [5]. The EAM potential has been extensively validated for metallic systems [4–7] and used in MD simulations of hydrogen

dissociation on nickel [7], self-diffusion of metals [6,5,8] and epitaxial growth [9]. A significant limitation of MD is its computational requirement since it explicitly accounts for thermal fluctuations. Thus, even with the use of parallel large-scale MD codes and a large number of parallel processors running over several days, simulations can only resolve time scales on the order of nanoseconds. Even accelerated MD methods such as hyperdynamics [10,11] and temperature-accelerated dynamics [12,13] are limited to small systems. Thus, an alternative method must be used to simulate phenomena over timescales on the order of seconds that are relevant to the electrodeposition process. The method used in this work is kinetic Monte Carlo (KMC) [14], which enables simulation over longer timescales with a much lower computational requirement.

Most of the previous research utilizing KMC to model the electrodeposition process has made use of the solid-on-solid (SOS) model developed by Gilmer and Bennema [15]. In the SOS model, the rates are a function of the number of occupied nearest neighbors with no vacancies allowed. The interaction energy of the atoms and the system are not computed since no interaction potential is considered. Hybrid multiscale simulation methods that blend the SOS technique (KMC) and continuum mechanics have been applied to model copper electrodeposition in trenches [16,17]. The SOS method has been applied to polycrystalline growth [18,19], facet growth [20] and two-dimensional growth [21–23]. However, a main drawback of the SOS model is that it does not accurately describe the metal crystalline microstructure, as is possible via MD using EAM potentials.

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The SOS method also does not account for vacancies, motivating Kaneko and co-workers [24–26] to introduce the solid-by-solid (SBS) method to address this limitation. However, the SBS method suffers from the same limitations as the SOS in that it does not accurately describe the microstructure of the metal crystal. Thus, structures obtained from SOS and SBS simulations are not always clearly related to a specific metal electrodeposition process.

In the present work, a KMC method (KMC-EAM) based on the highly descriptive EAM potential is presented which includes collective diffusion mechanisms (atom exchange and step-edge atom exchange), in addition to nearest-neighbor hopping. In past work, MD simulations using the EAM potential (MD-EAM) have been used only to predict activation energies for KMC simulations using the SOS and SBS models [27]. Unlike the approach used in the SOS and SBS methods, the EAM potential is used to form the Hamiltonian of the system in KMC-EAM simulations, not only to evaluate activation energies. More recent past approaches using the EAM potential directly in Monte Carlo simulations have shown promising results for the simulation of electrodeposition [28–31] including grand-canonical Monte Carlo and KMC simulations. Gimenez et al. [28] carried out KMC calculations using EAM potentials for two-dimensional deposition and limited the process to the growth of a single monolayer. Thus, these previous simulations were effectively limited to two-dimensional and sub-monolayer deposition dynamics.

In this work, the KMC-EAM method is applied to three-dimensional electrodeposition of a copper single crystal and validated by comparison with the equilibrium microstructures obtained by MD-EAM. The MD-EAM method relaxes a number of the constraints and assumptions of the KMC-EAM method: the on-lattice approximation, finite diffusion mechanisms, and temporal coarse-graining. The simulations are conducted over a range of current densities and temperatures that match common experimental conditions. Simulations are then performed within these parameter ranges to predict the effect of current density and temperature on surface morphology.

The paper is organized as follows: Section 2 – background on KMC and the EAM potential, Section 3 – presentation of the KMC-EAM method developed in this work, Section 4 – simulation results on the effect of current and temperature on the accuracy of the KMC-EAM method and Section 5 – conclusions.

## 2. Theory

### 2.1. Kinetic Monte Carlo method

In MD, the exact locations of the atoms are determined and their motion is solved directly via Newton's equations of motion. However, this is computationally expensive and so is limited to evolution of the domain over short time scales. For metallic systems, it can be assumed that atoms vibrate about specific locations in quasi-equilibrium over a period of time. Since each of these locations corresponds to a minimum in the potential energy of the system, an atom must overcome an energy barrier to move from one minimum to another [32]. Thus using a consistent fine-grained method, such as molecular dynamics or quantum mechanical density functional theory [32], the ground state lattice type (FCC, BCC, etc) and lattice spacing of a specific atomic system [6] are used as inputs for on-lattice KMC simulations. This is the basis of the on-lattice approximation of for conducting KMC simulations of metal deposition [32], whereby the metal atoms positions are limited only to sites on this crystal lattice.

Utilizing the on-lattice approximation, the discretized microscopic state  $\sigma$  of the system is a function of only lattice site occupancy and time where  $\sigma_i=0$  for a vacant site and  $\sigma_i=1$  for

an occupied site. In order to utilize the KMC methodology, an additional coarse-graining approximation must be used which assumes that the domain evolves through a discrete set of independent dynamic mechanisms. Furthermore, these dynamic mechanisms are assumed to be Poisson processes [14]. Given these approximations, the KMC method enables numerical solution of the master equation of the system where the probability density  $P(\sigma)$  of observing state  $\sigma$  is given as [14,32]:

$$\frac{dP(\sigma)}{dt} = \sum_{\sigma' \neq \sigma} G(\sigma' \rightarrow \sigma)P(\sigma') - \sum_{\sigma' \neq \sigma} G(\sigma \rightarrow \sigma')P(\sigma), \quad (1)$$

where  $G(\sigma \rightarrow \sigma')$  is the probability per unit time that the system will undergo a transition from  $\sigma$  to  $\sigma'$ . Alternatively, (5) is also known as the *chemical master equation* and may be reformulated as [33]:

$$d\sigma_i = \sum_j \Gamma_{ij}^+(\sigma) dt - \sum_j \Gamma_{ij}^-(\sigma) dt, \quad (2)$$

where  $\Gamma_{ij}(\sigma)$  is the transition probability ( $s^{-1}$ ) or propensity function for process  $j$  at site  $i$  when the state  $\sigma$  is observed. The term  $\Gamma_{ij}(\sigma)dt$  gives the probability of state  $\sigma$  undergoing a change due to some move  $j$  at site  $i$  within the time increment  $dt$  [34].

### 2.2. Embedded-atom method potential

The embedded-atom method potential is a semi-empirical potential that is based on density functional theory [4]. This potential closely describes the effect of metallic bonding in metal systems to accurately estimate the potential energy of an atom [5]. The potential is composed of both multi-body and pairwise contributions [4]:

$$E_i = F[\rho_i] + \frac{1}{2} \sum_{\substack{j \\ i \neq j}} \phi_{ij}(r_{ij}) \quad (3)$$

where  $r_{ij}$  is the distance between atoms  $i$  and  $j$ ,  $E_i$  is the interaction energy of atom  $i$ ,  $F$  is the multi-body *embedding energy* functional and  $\phi_{ij}(r_{ij})$  is a pair-wise repulsion between atoms  $i$  and  $j$ . The function  $\rho_i$  is the total host electron density for atom  $i$ :

$$\rho_i = \sum_{\substack{j \\ i \neq j}} \rho_h(r_{ij}) \quad (4)$$

where  $\rho_h$  is a function that quantifies the electron density of a neighboring atom. The EAM parameters are estimated by fitting the EAM potential to known experimental values of metal properties such as the lattice constant, elastic constants, sublimation energy, and vacancy-formation energy [4,6,5,7].

## 3. Methodology

The example chosen to apply and assess KMC-EAM in this work is copper electrodeposition onto a copper substrate (working electrode) from an acidic sulfate solution. The overall reaction for the cathodic reduction of  $Cu^{2+}$  is:



$Cu^{2+}$  ion reduction proceeds through consecutive single-electron transfer steps and involves the formation of an intermediate in which Cu has oxidation state +1 [35,36]. However, numerous studies have shown that the first of these steps has much slower

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