Growth of Cu on Ag (001) at Experimental Deposition Rates Using TAD

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ABSTRACT

The initial stages of growth of (001) Cu films on (001) Ag substrates have been investigated using the temperature accelerated dynamics (TAD) method. The acceleration provided by this method made it possible to simulate the deposition of Cu on (001) Ag at 77 K using a deposition rate of 0.04 ML/s, which matched previously reported experiments of Egelhoff and Jacob. These simulations were achieved without *a priori* knowledge of the significant atomic processes. The present TAD simulation results showed that the increased lattice parameter in the film plane of the pseudomorphic Cu reduces the activation energy for the exchange mode of surface diffusion, allowing the formation of compact Cu islands at 77 K. Furthermore, the TAD simulations showed that the in-plane lattice expansion promoted some complex surface diffusion processes.

Keywords: molecular dynamics, surface diffusion, thin films, copper, silver.

1 INTRODUCTION

Conventional molecular dynamics (MD) simulations can be very useful for studying atomic processes, such as energetic particle impacts, occurring on short time scales. However, computational stability requires that MD simulations be performed with integration steps no longer than several femtoseconds. This limits the total simulated time for most cases to less than several nanoseconds. For this reason, most MD investigations of thin film deposition processes have employed effective deposition rates on the order of 10^9 monolayers per second, which are factors of 10^8 to 10^{11} higher than experimental deposition rates. Since thermally-activated atomic processes such as surface diffusion, occurring with characteristic waiting times of microseconds to milliseconds can significantly affect the development of film structures, conventional MD simulations cannot fully model such film growth.

One approach to this dilemma is to create a catalog of the activation energies and kinetic prefactors for all significant thermal processes and to use this catalog in a kinetic Monte Carlo (KMC) simulation of the system of interest. In systems with any degree of complexity, however, it is difficult to *a priori* create a sufficiently complete catalog of atomic processes. This problem is especially severe for processes with near-threshold activation energies at the temperature of interest. For these processes, local variations in atomic environments can produce large variations in reaction rates.

An alternative approach to simulating processes over time scales of several seconds is provided by the temperature-accelerated dynamics (TAD) method of Sørensen and Voter [1]. As briefly described in the following section, TAD uses a combination of molecular dynamics and statistical thermodynamics to correctly follow the actual dynamics of a system while providing accelerations of up to 10^9 in the calculations. This is achieved without any *a priori* knowledge of the relevant atomic processes. With an appropriate selection of conditions, this technique can allow the simulation of early stages of film growth at experimental deposition rates.

In the present investigation, TAD was applied to study the growth of Cu on Ag (001) at 77 K. The conditions were chosen to duplicate the experiments of Egelhoff and Jacob [2]. The Egelhoff and Jacob results were of interest because they had observed persistent RHEED oscillations for several depositions at 77K, at which they did not expect significant thermal surface diffusion. They interpreted the RHEED oscillations as indicative of quasi-layer-by-layer growth, which they attributed to transient mobility of deposited atoms. In the case of Cu deposited on Ag (001), the oscillations were especially strong. In addition, they inferred island sizes approximately 10 atoms across from the width of LEED spots from the film. Although Egelhoff and Jacob's conclusions were later questioned by Evans, et al. [3], among others, the possibility that the in-plane tensile strain induced in Cu by pseudomorphic growth on Ag (001) could affect the Cu migration mechanisms made this an interesting system to investigate by TAD.

2 SIMULATION DETAILS

As described in detail by Sørensen and Voter [1], the TAD method makes use of the fact that the rate at which any thermally-activated process occurs can be increased by

simply increasing the temperature of the system under study. This acceleration comes from the well-known Arrhenius relation:

$$Rate = \nu_0 \bullet \exp\left(\frac{-E_A}{kT}\right),$$

where ν_0 is the rate prefactor, E_A is the activation barrier energy, k is Boltzmann's constant, and T is the absolute temperature. This relation also shows, however, that a temperature increase will not increase the rates of processes with different activation barriers by the same amount. Thus a simple temperature increase will not correctly preserve the system dynamics at the base temperature.

The TAD method addresses this problem by first performing a "basin-constrained" simulation at an increased temperature. In this simulation, MD is performed at the elevated temperature until a transition is detected. The activation barrier for this transition is then determined, the time when it would have occurred at the lower system temperature is calculated, and the simulation is continued in the original basin. Once sufficient statistics have been accumulated to determine which event would have occurred first at the lower temperature, that transition is accepted, the system is transformed to the new basin, and the process is continued. An extension of this technique is required in the case where a sequence of low-barrier transitions occurs many times (perhaps millions) during the evolution of the system. To avoid unnecessary computational work, such transitions are handled by KMC, once their statistics are sufficiently established. To perform a TAD simulation of film growth, the deposition of a single atom is first simulated by conventional MD for the first few picoseconds. The system is then evolved by TAD until the time for the next atom deposition in the calculation cell. The process is repeated until the desired amount of deposition is achieved.

To duplicate the conditions of Egelhoff and Jacob [2], the present simulations were performed at a system temperature of 77 K for an average deposition rate of 0.04 monolayers per second. The high temperature used to accelerate the system was 550 K. The calculation cell comprised 98 atoms per (002) layer, with a substrate of 7 of these Ag layers. The cell was periodic in the film plane and had 4 active layers, the bottom of which was thermostatted. A total of 147 Cu atoms (1.5 ml) was deposited and all transitions were recorded. The atomic interactions were modeled by the embedded-atom (EAM) potentials of Voter and Chen [4].

3 RESULTS AND DISCUSSION

As seen in previous experimental investigations [2,5], the Cu deposit in the present study was pseudomorphic with the Ag substrate, taking on the Ag lattice parameter in the film plane. This 13% Bain distortion in the Cu deposit shrinks the out-of-plane lattice parameter, such that the Cu structure is essentially body-centered cubic. A number of theoretical studies [6,7] have shown that the bcc Cu structure is unstable, but it can be maintained for sufficiently thin films on a suitable substrate. The distortion of the Cu crystal structure also has dramatic effects on surface diffusion mechanisms. This can be illustrated by nudged-elastic-band [8] calculations of the activation barriers for the <110> surface hop and the <100> surface exchange movement of a Cu atom on a strained (001) Cu surface. This calculation was performed for a Cu slab of 3 active and 5 fixed layers with up to 15% biaxial tensile strain imposed in the plane of the slab. As shown in Figure 1, the strain increases the barrier for the hop by a maximum of approximately 30%, while it decreases the barrier for the exchange by up to a factor of 4. The calculation also showed that there was a 5 - 18 meV secondary minimum along the exchange path for strains greater than 10%.

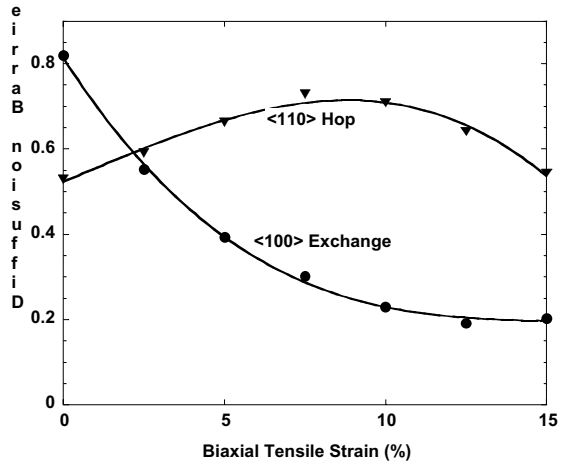
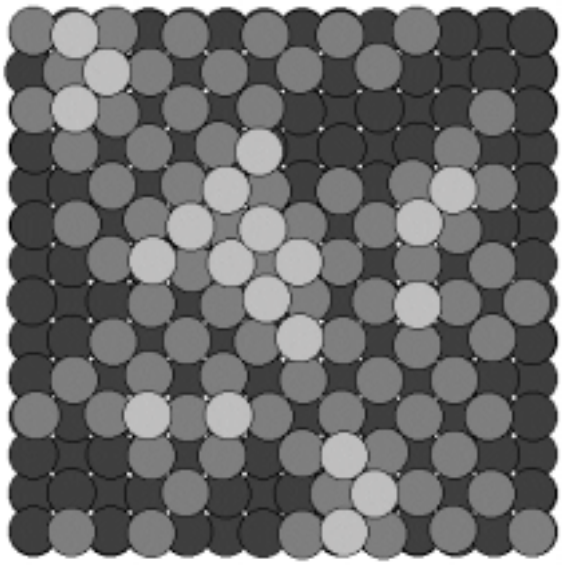
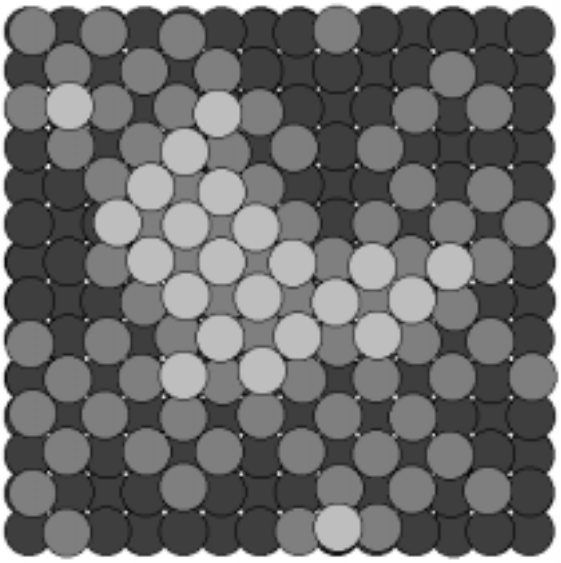


Figure 1. Activation barriers for the hop and exchange mechanisms for diffusion of a single Cu atom on a 3-layer strained (001) Cu film.

The TAD simulation showed that the reduced activation barriers for exchange events allowed short-range thermal migration of atoms deposited in the second and third layers of the Cu film deposited on Ag. The net effect of this increased diffusion is illustrated in Figures 2 and 3, which compare films simulated by conventional MD at 5 x 10^9 ml/s and TAD at 4 x 10^{-2} ml/s. The same set of randomly-selected deposition positions was used in both simulations. The additional thermal diffusion allowed in the TAD simulation produced noticeably more compact terraces in film layers above the first at both 1 and 1.5 ml total Cu deposition. The differences between the two simulation methods for the first film layer are much less pronounced. This is expected, since the activation barriers for the hop and exchange barrier of Cu on (001) Ag are 0.62 and 0.52 eV, respectively, for the Voter and Chen EAM potentials. Thus these mechanisms would not be activated at 77 K.



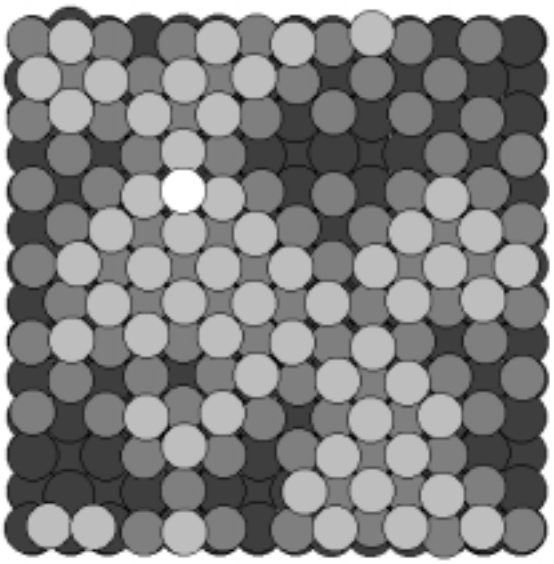
(a)



(b)

Figure 2. Simulated Cu films with 1 ml total deposition on (001) Ag at 77 K for (a) conventional MD (5 x 10^9 ml/s) and (b) TAD (4 x 10^{-2} ml/s). The darkest atoms are the Ag substrate, and the 2 lighter shades of gray are Cu atoms in the first and second film layers.

With the exception of a few atoms that were deposited in overhanging sites at terrace edges, all observed thermally-activated diffusion events were by atom exchange. For atoms which initially had no nearest neighbors in the first Cu terrace, the exchange barriers ranged from 0.13 to 0.20 eV.



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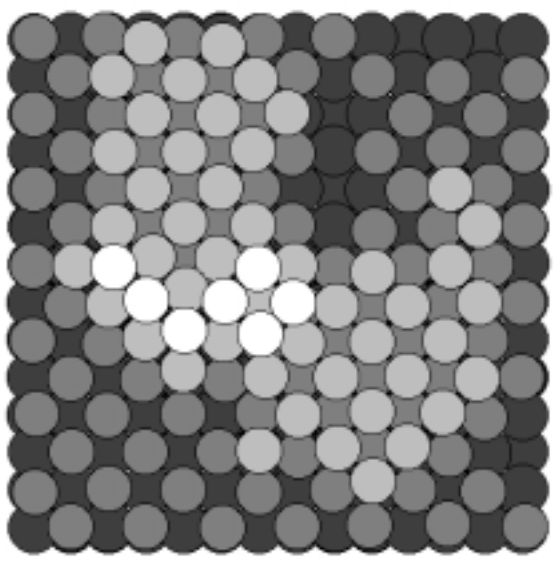

(b)

Figure 3. Simulated Cu films with 1.5 ml total deposition on (001) Ag at 77 K for (a) conventional MD (5 x 10^9 ml/s) and (b) TAD (4 x 10^{-2} ml/s). The darkest atoms are the Ag substrate, and the 3 lighter shades of gray are Cu atoms in the first, second, and third film layers.

Without allowing for possible variations in prefactors, this barrier range represents a factor of 3.8 x 10^4 in average reaction rate, depending on local atomic environment. For atoms which initially had a nearest neighbor in the first Cu terrace, the range of observed barriers was even greater, from 0.02 to 0.17 eV. The existence of the very low-barrier

events proved the value of the KMC modification to the TAD code, noted in Sec. 2.

Some interesting and unexpected diffusion mechanisms were observed for atoms deposited initially on the second Cu terrace. One example is the 3-level exchange process shown in Figure 4, which removed atoms from the third Cu terrace. By a combination of exchanges from terrace 3 to 2, 2 to 1, and 1 to 2, this mechanism produces an effective vertical atom movement of one layer and an effective lateral atom movement of about 0.6 nm. The specific event shown in Figure 4 had an activation barrier of only 0.09 eV.

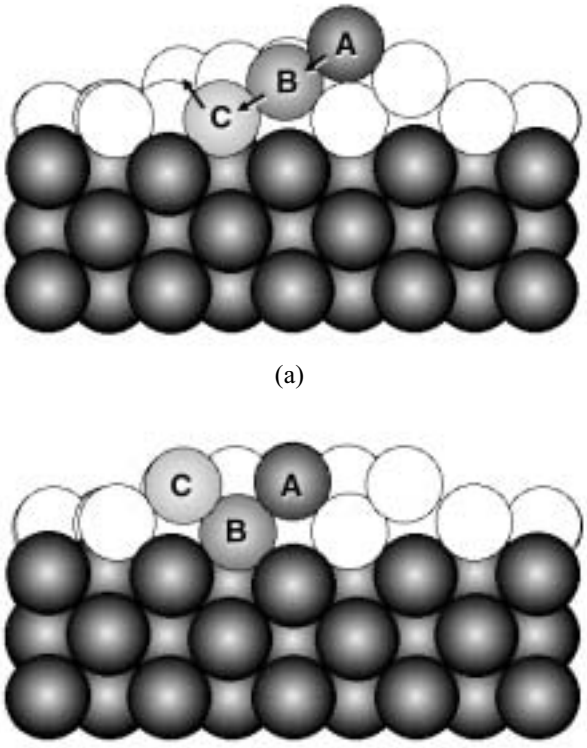

Figure 4. Cross-section view of a 3-level exchange process that removes an atom from the third film terrace and adds an atom to the second; (a) initial configuration, showing directions of atom movements; (b) final configuration.

Another interesting feature observed for atoms on the third film terrace was the occupation of intermediate off-lattice configurations along an exchange path. As noted above, these configurations were observed to have shallow energy minima for an atom on a full 3 monolayers of strained Cu. In the TAD simulation, the relative energies of the 3 states along this reaction path varied considerably, depending on the terrace size and the position of the third-layer atom. In fact, the intermediate off-lattice configuration was observed to be the lowest energy state for some cases.

The present TAD simulation results show that the lowered activation barriers for surface exchange processes on Cu (001) that are induced by deposition on Ag (001) allow short-range terrace diffusion and inter-terrace transport at temperatures near 77 K. These processes produce compaction of the Cu islands and a film structure that resembles that which Egelhoff and Jacob inferred from their RHEED and LEED experiments. The observed island compaction was achieved with a relatively small amount of atom mobility. If we look at the distribution of final atom positions after 1.5 ml of deposition relative to the initial deposited atom positions, 49 atoms moved laterally more than 0.2 nm, the single exchange distance, and the largest lateral atom movement was less than 0.6 nm.

4 SUMMARY AND CONCLUSIONS

Temperature-accelerated dynamics (TAD) simulation has been applied to study the growth of a Cu film on Ag (001) at a temperature of 77 K and a deposition rate of 0.04 ml/s. Several surface exchange diffusion mechanisms were observed during the growth of a 1.5 ml film under these conditions. These diffusion processes produced compaction of Cu islands and a significantly different film microstructure from that produced in a conventional molecular dynamics (MD) simulation of the same deposition. The wide range of activation energies for similar mechanisms would make it very difficult to simulate this system by a kinetic Monte Carlo method that requires an *a priori* knowledge of the kinetics for all atomic processes.

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