Multiple Time Scale Simulations of Metal Crystal Growth Reveal the Importance of Multiatom Surface Processes

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A method for extending atomistic computer simulations of solids beyond the nanosecond time scale was used to simulate metal crystal growth on the time scale of laboratory experiments. Transitions involving concerted motion of multiple atoms on the crystal surface are found to lead to remarkably smooth growth of pure Al(100). Cu(100) is found to grow with a rougher surface, consistent with experiments. Not only is the activation energy of the multiatom Al processes surprisingly low, but vibrational entropy also favors processes where many atoms are displaced.

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Computer simulations of the arrangement and motion of atoms can reveal a great deal of information and add insight into a wide range of phenomena in chemistry, condensed matter physics, and materials science, especially where experimental measurements are difficult to perform or hard to interpret. A major limitation of such simulations, however, is the short time scale that can be simulated by conventional techniques. Atoms vibrate on a time scale of femtoseconds, but most important, chemical reactions or diffusion events in solids take place on a much longer time scale, on the order of milliseconds or more — a disparity exceeding 10 orders of magnitude. Well known methods can be used to solve Newton's equations (assuming a classical description of the system is accurate) but even if the interaction between the atoms is approximated in a simple way, direct classical dynamics simulations can span less than a microsecond after several weeks of computations on today's computers. There is, therefore, a large gap between the time scale that can be simulated with direct classical dynamics methods and the time scale of interesting atomic events one would like to be able to study by computer simulations.

Fortunately, many systems have a natural separation of time scales. When the time evolution of a system can be characterized as a sequence of well defined transitions separated by extended time periods in each one of the intermediate states, then the fast atomic vibrations can be treated statistically and the rate of the transitions estimated using transition state theory (TST) [1,2]. Within TST the rate of a chemical reaction is estimated by identifying the most difficult region of configuration space the system must reach during a transition — the so-called "transition state." In the case of solid systems such as the ones investigated here, the vibrational motion of the atoms is confined to rather small regions around well defined average positions. Then, the harmonic form of TST (HTST) is a good approximation to full TST and the rate constant is given by [3,4]

$$k^{\mathrm{hTST}} = \frac{\prod_i^{3N} \nu_i^{\mathrm{init}}}{\prod_i^{3N-1} \nu_i^{\ddagger}} e^{-(E^{\ddagger}-E^{\mathrm{init}})/k_B T}. \tag{1}$$

Only the saddle point energy, $E^{\ddagger}$, the energy of the minimum, E^{init}, and the normal mode vibrational frequencies at these atomic configurations, ν_i, are needed to estimate the rate. The exponential term typically dominates the rate so processes with high barriers are unlikely to occur. The factor in front of the exponential, the prefactor, is a measure of the relative entropy at the minimum and the saddle point regions. In a typical atomic scale system, the hardest part of calculating a rate with HTST is locating the position of the saddle points because of the large number of degrees of freedom.

In situations where all the relevant transitions a system can undergo are known beforehand, the time evolution can be simulated using the kinetic Monte Carlo (KMC) method [5–7]. There, a list is constructed of all the possible transitions from a given initial arrangement of the atoms. Random numbers are then used to choose a transition from the list according to the relative transition rates. The system is advanced to the final state of the chosen transition and, on average, the simulation time is advanced by the inverse of the sum of the rates of all possible transitions. The list of possible transitions is then updated and the cycle repeated.

Traditional implementations of KMC assume that atoms sit in lattice sites and only a few, predetermined transition mechanisms are included. Typically one atom is assumed to move and the rates of possible transitions are determined from the local environment around the moving atom. Even with this simple strategy the number of different local environments around a single atom grows exponentially with the number of neighbors included. A typical predetermined KMC list includes a few tens of processes and is severely limited in the variety of possible transitions. Furthermore, there is no guarantee that the transitions which seem likely to the modeler are indeed the relevant processes in the system.

A warning comes from studies of adatom diffusion on the (100) surfaces of fcc metals. Until 1990 it had been assumed that an atom diffusing on the surface hops from one site to an adjacent site. Theoretical calculations [8] and experimental measurements [9,10] on Al(100), Pt(100), and Ir(100) surfaces, however, showed that the adatom can more easily diffuse by two-atom concerted displacement where the adatom replaces a surface atom which in turn becomes an adatom [8]. This example illustrates the need for simulation methodology where possible transitions are found in some systematic way from the atomic forces rather than simply by assuming the transition mechanism *a priori*. One solution is temperature accelerated dynamics (TAD) [11], in which each transition is selected after a brief evolution at high temperature. TAD has been applied to metal growth problems similar to those we discuss below [12]. Alternatively, we have shown one can maintain the KMC framework but eliminate the need for the predefined event table and lattice approximation [13]. Given a state of the system, we search for saddle points starting in various randomly chosen directions. The search method [14] relies on a scheme for estimating the lowest curvature mode on the potential energy surface at a given configuration of the atoms. The potential energy is then maximized in the direction of this mode and minimized in all other directions. In this way, a minimization of an effective force leads to saddle points on the potential energy surface.

This method has been applied to study the mechanism by which an adatom diffuses on the Al(100) surface [14]. Interactions between atoms were described with an embedded atom (EAM) potential function [15]. The three lowest energy processes found were the two-atom concerted displacement [8], the hop, and a four-atom concerted displacement shown in Fig. 1(a). In order to verify the accuracy of the EAM potential function, we have now calculated the rate of these and several other processes within density functional theory (DFT) [16] using the VASP [17] code and the nudged elastic band method [18]. The lowest energy, two-atom concerted displacement has a barrier of 0.23 eV with the EAM description and 0.24 eV in DFT. The calculated rate of the four-atom concerted displacement process also shows good agreement between the EAM and DFT calculations [see the inset in Fig. 1(a)]. In contrast, both EAM and DFT calculations predict that a Cu adatom on a Cu(100) surface diffuses by hops — the activation energy for the two-atom concerted exchange is about a factor of 2 larger [19].

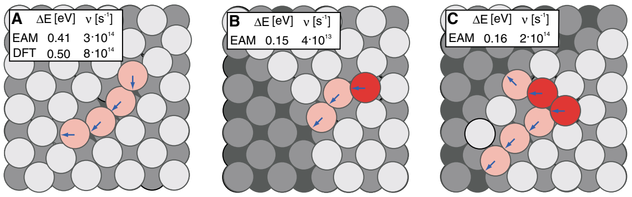

FIG. 1 (color). Multiatom processes seen in aluminum crystal growth simulations at 80 K include the four-atom concerted displacement process (a). The most commonly observed adatom descent process (b) also involves concerted displacement of several atoms. More than 20% of the activated processes involved three or more atoms such as the six atom concerted descent process shown in (c).

In the long time scale simulations reported here, the growth of aluminum and copper crystals with (100) surface orientation was studied during vapor deposition as a function of surface temperature in the range from 0 to 80 K. Thin overlayers of these metals are extensively used, for example, as interconnects in semiconductor devices. Initially, the system was a slab consisting of six layers of atoms, 128 atoms per layer, with the bottom two layers frozen to mimic the confining effect of deeper layers not included in the simulation. Up to 12 layers of atoms were deposited onto the surface at normal incidence with an incident kinetic energy of 0.1 eV at rates from 0.1 to 10 monolayers (ML) per second. Experimentally achievable deposition rates cannot be reproduced by direct classical dynamics simulations because of the time scale problem mentioned above. Instead, we use a multiple time scale simulation approach in which the deposition events are simulated with classical dynamics over a 2 ps time period, sufficiently long for the heat generated at impact to dissipate [20]. Then the time interval between deposition events, on average 1 to 100 ms, is simulated with the extended KMC method where thermally activated processes are found by saddle point searches [13].

In order to carry out these types of simulations, an implementation of distributed computing was developed [21] using an approach similar to the popular seti@home screen saver. A server computer keeps track of the state of the system being simulated and distributes saddle point searches to a couple of hundred Windows and Linux client computers to take advantage of idle time. The saddle point searches are started by choosing an undercoordinated atom at random and then displacing it and its first and second nearest neighbors (typically 10 to 15 atoms) using a Gaussian distribution of width 0.2 Å. All atoms except those in the bottom two layers are movable during the saddle point search.

After a successful search, the clients report the energy and atomic configuration of the saddle point to the server. The server creates a list of transitions the system can undergo, including a deposition event, and a transition is selected based on random numbers. If the deposition event is chosen, the server heats the system to the surface temperature being simulated and deposits an atom starting 8 Å above the surface. It is important to simulate the deposition event to include steering effects [12,22] and dynamical processes due to local heating. In the Al simulations, 35% of deposition events caused some rearrangement of surface atoms of which 20% resulted in a smoother surface. After a deposition event or an activated process is simulated, the system is brought to the closest potential energy minimum by rapid quenching, and the minimum configuration passed on to available clients to carry out new saddle point searches.

In the crystal growth simulations presented here, saddle point searches were continued until 150 searches had been successful, revealing on average 50 distinct possible transitions. A search was considered successful if (i) the atomic forces dropped below 0.001 eV/Å, (ii) a normal mode analysis yielded one negative curvature mode, and (iii) energy minimization led to the atomic configuration corresponding to the current state of the system. The deposition of ten layers at 80 K involved ca. 2000 distinct activated transitions and could be simulated in three weeks using several cumulative years of client CPU time. In 85% of the cases, the lowest energy process was found more than once suggesting (but there is no guarantee) that the dimer searches found the lowest energy processes available to the system most of the time.

This methodology was tested by simulating the growth of a Cu(100) surface, a system that has been studied extensively. A deposition rate of six layers per minute was used to match experimental measurements of reflection high-energy electron diffraction (RHEED) [23]. The RHEED intensity oscillates as layers are added to the crystal and the height of the peaks indicates how smoothly the surface is growing. A RHEED signal was calculated with a commonly used approximation [24] for the simulated deposition of eight layers and compared with the experimental measurements. The height of the RHEED peaks was found to decay exponentially with the number of deposited layers with a decay constant of 1.0 ML^{-1}, in excellent agreement with experiments.

We also simulated Al(100) growth, a system which has not been studied much experimentally. Contamination and oxidation problems are severe on aluminum surfaces making such measurements difficult [25]. Our simulations indicate that clean Al(100) grows remarkably smoothly. The filling of successive (100) layers at 80 K is shown in Fig. 2. Perfect layer-by-layer growth would manifest itself as a series of straight, parallel lines. The aluminum results deviate only slightly from that. In contrast copper layers are far from being complete when new layers form. After the equivalent of five layers of atoms have been deposited, there are five exposed layers on the Cu(100) surface. Another way of measuring the surface roughness is the height-height correlation function [26] shown in the bottom panel of Fig. 2. Again, aluminum shows almost perfect layer-by-layer growth. The oscillations in the aluminum roughness are caused by the unavoidable roughness of a partially filled layer. In contrast, the roughness of the copper surface increases steadily.

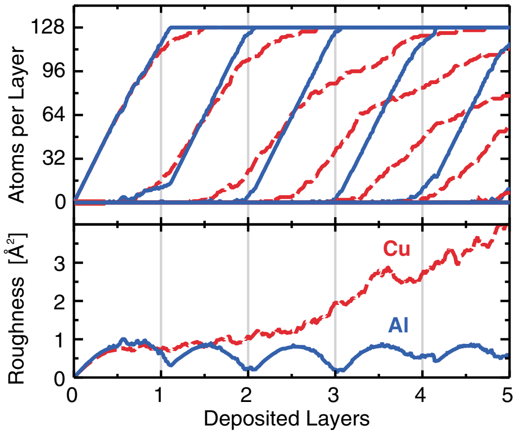

FIG. 2 (color). The upper panel shows the number of atoms in each deposited layer; the lower panel gives roughness [26].

The growth of copper and aluminum has distinctly different dependence on surface temperature. Figure 3 shows the roughness of the crystal surfaces averaged over the deposition of the fifth layer. When the atoms are deposited onto a surface at 0 K, the roughness of the two metal surfaces is similar. As the surface temperature is increased, the Cu surface becomes rougher while the Al surface becomes smoother. Such an increase in roughness with temperature has been observed experimentally for Cu(100) [23] and has been explained by the increase in compact island size which leads to increased probability of atoms landing on top of existing islands [26]. The smoothness of the growing Al(100) surface results from thermally activated processes that bring adatoms down from atop islands. These processes involve concerted displacement of two or more atoms, as illustrated in Fig. 1. Analogous to the Al adatom diffusion on the flat surface, where both DFT and EAM calculations show that multiatom

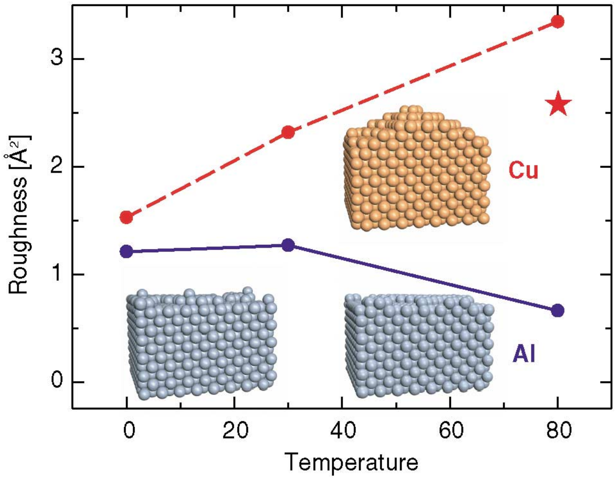

FIG. 3 (color). Temperature dependence of the roughness of aluminum and copper surfaces after five layers have been deposited at ten layers per second. At low temperature the two metals have similar roughness, but as the surface temperature is increased and long time scale processes become active, copper becomes rougher while aluminum grows smoother. At the slower deposition rate of six layers per minute used in the experiments of Egelhoff and Jacob [23] the copper surface (★) grows smoother with more prevalent activated events.

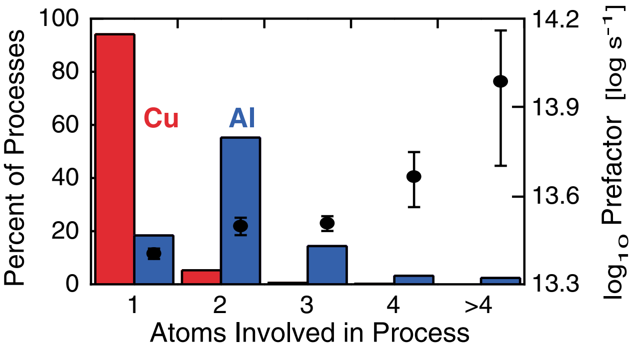

FIG. 4 (color). Most surface transitions observed in simulations of aluminum growth at 80 K involve two or more atoms, while single atom processes are most common in Cu. The transition rate has a larger prefactor, i.e., more favorable entropy contribution, when more atoms are involved in the process (see filled circles and the vertical axis to the right).

concerted displacements have low activation energy and a large prefactor, the multiatom down-stepping processes are much more facile on the aluminum surface (activation energy ca. half as large). Descent at kink sites is particularly important even when the adatom starts two sites away from the kink and the process involves concerted motion of three atoms [Fig. 1(b)]. Even a process where two atoms descend simultaneously from atop an island, a concerted displacement involving six atoms [Fig. 1(c)], has activation energy of only 0.16 eV, substantially smaller than the adatom diffusion on the flat surface, 0.23 eV. In our growth simulation, more than 20% (see Fig. 4) of the activated processes found for aluminum are descent processes involving three or more atoms. These multiatom descent processes lead to smoother growth because atoms can more easily descend from atop islands, preventing the formation of three-dimensional islands. In contrast, most of the transitions that occur in the copper growth simulation involve only one atom, as shown in Fig. 4.

Another factor which contributes to the large number of multiatom processes in aluminum, besides the low activation energy, is the large prefactor. In fact, we have found that the prefactor tends to be larger the more atoms are displaced in the transition, as shown in Fig. 4. This is perhaps surprising since one could argue that as more atoms need to move in a concerted way, the system has more constraints and the entropy at the transition state becomes smaller, resulting in a smaller prefactor. But, the fact is that more vibrational modes have low frequency at the saddle point configuration when more atoms are displaced in the transition. Each atom that is displaced becomes less tightly bound at the saddle point, leading to soft vibrational modes and thereby increasing the vibrational entropy at the transition state.

The remarkably smooth growth of the Al(100) surface we have observed in our simulations could have useful consequences, if verified by experimental measurements. When a smooth metal coating is needed on a cool surface, clean aluminum could work well while, for example, copper would not be as good a choice.

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