

## Accelerated Molecular Dynamics of Thin Film Growth

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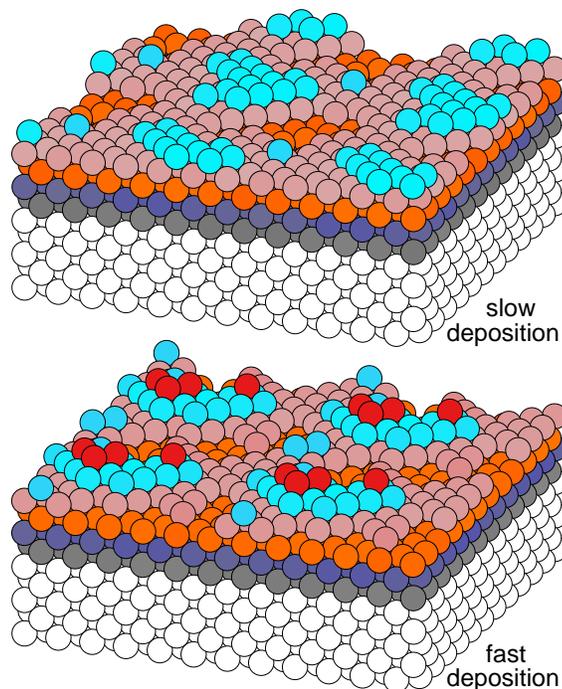
Thin film growth is important to a wide range of technologies, and it is usually of interest to optimize or control film properties such as roughness, strength, friction resistance, adhesion to the substrate, etc. This can be a daunting task, consuming substantial experimental resources, due to the intrinsic complexity of the film growth process. The growth characteristics of a seemingly simple homoepitaxial system such as Cu/Cu(100) are sufficient to illustrate this complexity. At high temperatures, where the surface diffusion is very fast relative to the deposition rate, vapor deposition leads to a smooth film, as expected. As the deposition temperature is lowered, the film becomes rough, also as expected. However, as temperature is lowered further, the film becomes smooth again! This effect, first discovered 10 years ago and since observed in many other systems, is referred to as reentrant layer-by-layer growth, and arises from a delicate interplay of the rates for atomic diffusion and reorganization events. Finally, at very low  $T$ , the film exhibits the stochastic roughness that is expected when diffusion is negligible.

Until now, most atomistic simulations of epitaxial surface growth have relied on one of two techniques: molecular dynamics or kinetic Monte Carlo. While molecular dynamics is exact (for a given empirical potential energy function), its timescale is limited by the atomic vibrational period (femtoseconds), so that simulations as long as  $1\mu\text{s}$  require heroic efforts, while still falling several orders of

magnitude short of typical deposition rates. On the other hand, kinetic Monte Carlo employs a tabulated “catalog” of possible diffusion events which may occur, so its timescale is determined by the fastest event in the catalog and simulation times on the order of seconds or minutes are not uncommon. However, the restriction of possible events to those in the predefined catalog raises questions about the potential importance of novel mechanisms that may have been omitted.

Recently, two new methods (described in previous issues of this publication) have been introduced for accelerating the dynamics of rare events such as the diffusion processes which occur between deposition events. The first, hyperdynamics [1], modifies the potential energy surface by adding a bias potential  $\Delta V_b(\mathbf{r})$  in potential energy basins to accelerate the escape rate from these basins, while maintaining the correct relative escape rates for multiple channels, and allowing the elapsed time to be accumulated as a statistical property. The second, parallel replica dynamics [2], involves running  $N$  independent trajectories on  $N$  processors until an event is detected on any processor, at which time all processors are notified and  $N$  new trajectories are started in the new potential basin.

By combining these two methods, and running  $N$  independent *hyperdynamics* trajectories on  $N$  processors, a multiplicative computational boost can be achieved, pushing the timescale into the millisecond regime and beyond. We have exploited this to study the vapor deposition of Cu on a



**Figure 1: Snapshots from the growth of Cu on Cu(100) at  $T = 300\text{ K}$ , after 4 monolayers (colored atoms) have been deposited at rates of one atom every  $100\text{ ns}$  (1 monolayer /  $7.2\ \mu\text{s}$ , top panel) and one atom every  $10\text{ ps}$  (1 monolayer /  $720\text{ ps}$ , bottom panel).**

Cu(100) surface at deposition rates which approach experimental ones. Individual deposition events are carried out with ordinary molecular dynamics on a single processor for a few picoseconds, just long enough to allow the deposition energy to dissipate (particularly important for hyperthermal depositions involving 10–100 eV). The system configuration is then broadcast to all processors, which run a short period with periodic momenta randomizations to decorrelate the parallel replicas, and then begin accumulating simulation (hyper-) time. Snapshots from two runs at  $T = 300$  K with deposition rates differing by  $10^4$  are shown in Figure 1 where the actual system (72 atoms per layer) has been replicated in the lateral directions for clarity.

At the slower deposition rate, which is inaccessible by ordinary molecular dynamics, the growing film is noticeably smoother. By carrying out a series of such simulations in which the temperature and deposition rate is varied, we have observed what we believe is the onset of reentrant layer-

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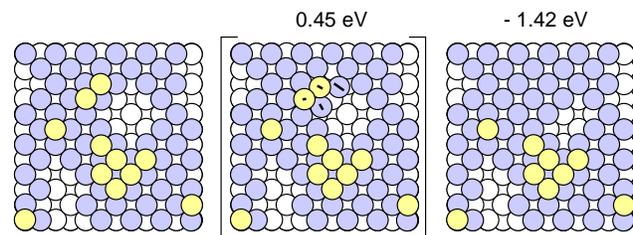
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by-layer growth as temperature is increased and/or the deposition rate is slowed. Another parameter which influences surface morphology is the deposition energy; preliminary simulations suggest energies near 30 eV can optimize the surface smoothness.

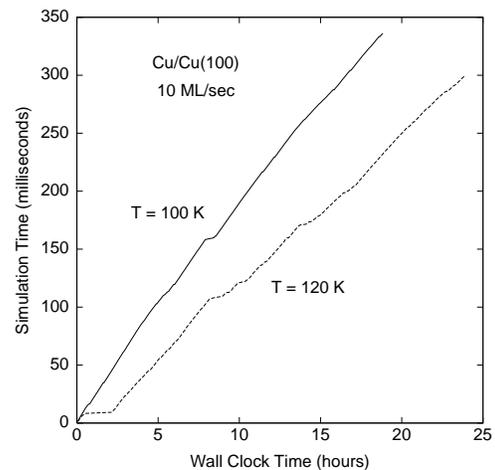
An example of a concerted mechanism which would almost certainly be omitted from a kinetic Monte Carlo catalog, but which occurs naturally in a hyperdynamics/parallel replica dynamics simulation, is shown in Figure 2. Here a total of four atoms are involved as a dimer exchanges down into the first layer, with a barrier even lower than that for terrace diffusion.

As the temperature is decreased, the larger instantaneous hyperdynamics boost ( $\Delta V_b(\mathbf{r})/kT$ ) as well as the decreased frequency of events permit simulations over even more impressive timescales. For example, the nonlinear evolution of “boosted” simulation time at  $T = 100$  K and 120 K (temperatures still well above the liquid nitrogen  $T = 77$  K at which many surface science experiments are carried out) is illustrated in Figure 3. Here we are simulating thermal

vapor deposition on a Cu(100) surface at 10 monolayers per second, comparable to some of the faster experimental deposition rates currently used. These simulations were performed on 1200 ASCI Red processors, with each run reaching 0.3 seconds of simulation time (3 monolayers) in less than a day. For comparison, a 24-hour simulation using a conventional (serial) molecular dynamics code on the fastest workstation available today would only accumulate 20 to 30 nanoseconds, *seven orders of magnitude* less than the simulations in Figure 3.



**Figure 2: A 4-atom concerted event observed during our simulations, typical of the mechanisms which kinetic Monte Carlo catalogs would omit. The central image shows the saddle point, with heavy lines indicating the reaction coordinate (eigenvector with imaginary frequency).**



**Figure 3: Boosted simulation time for two Cu/Cu(100) deposition runs on 1200 ASCI Red (333 MHz Pentium II Xeon) processors.**

[1] A. F. Voter, *J. Chem. Phys.* **106**, 4665 (1997); *Phys. Rev. Lett.* **78**, 3908 (1997).

[2] A. F. Voter, *Phys. Rev. B* **57**, 13985 (1998).

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