Molecular Dynamics Investigation of the Rapid Diffusion of Very Large Heteroepitaxial Islands

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Even when created in carefully controlled conditions, surfaces of crystalline solids do not consist of perfectly ordered rows of atoms. They are rather akin to a flatland populated by a whole ecosystem of defects like adatoms (isolated atoms standing on the surface), vacancies, islands (small groups of bound adatoms), pits, steps (partially filled layers), or dislocations. The way these defects move and interact with each other controls the static and dynamic properties of the surfaces, which are in turn crucial to technological applications like epitaxial film growth or heterogeneous catalysis. Traditionally, it has been assumed these surfaces evolved mainly through the repeated motion of single defects (i.e., adatoms or vacancies). More recently, practitioners in the field realized that more complex defects like islands can also move coherently through mechanisms such as glide [1], dislocation [2], or reptation [3]. However, these mechanisms are thought to apply mainly to relatively small defects. In this work, we simulated the evolution of a heteroepitaxial metallic system and discovered a new mechanism by which islands of unexpectedly large size can rapidly diffuse. We show that such a large island can actually diffuse orders of magnitude faster than a single adatom, thus demonstrating that the evolution of surfaces can, in some cases, be significantly affected by the movements of large defects.

We consider the case of an island of 169 silver atoms resting on an otherwise perfect copper (001) surface (Fig. 1). The island is taken to adopt a compact hexagonal shape reconstructing into a (10x2) unit cell as observed experimentally [4]. This reconstruction is driven by the large size mismatch between Ag and Cu. The evolution of this system was simulated at temperatures between 300K and 225K using molecular dynamics (MD), while we resorted to an accelerated dynamics method developed at LANL by one of us (namely the Parallel Replica Dynamics method [5]) to access the very long time scales required to observe movement of the island at temperatures down to 175K.

The most surprising feature of our simulations is that, despite its very large size, the island is able to hop (jump to a neighboring stable site) on the surface very rapidly, even at low temperatures. These results are presented in Fig. 2, where the hopping rate of the island is reported as a function of temperature. To put these results in perspective, the hopping rate of a single silver adatom on the same

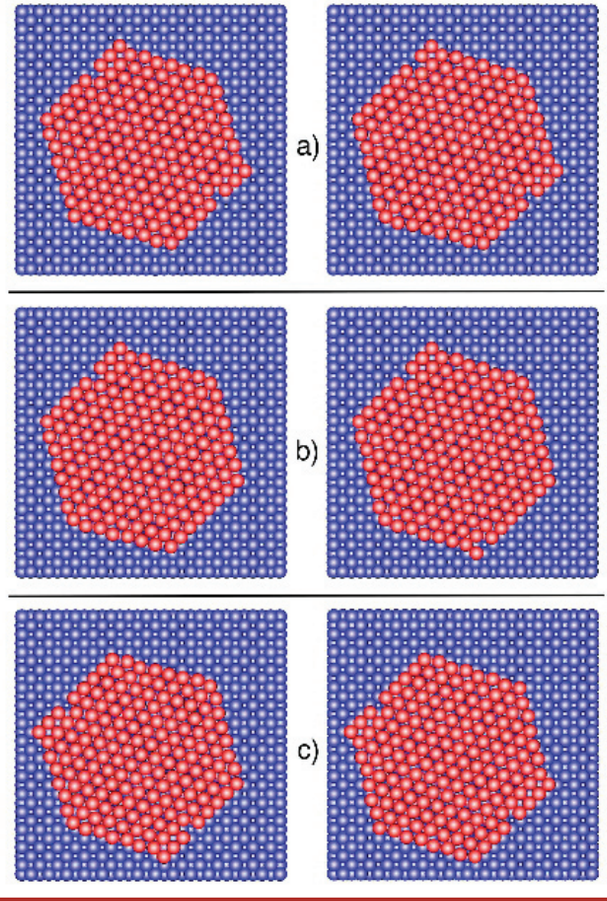

Fig. 1. Various conformation changes observed during a hop of the island: a) simple vacancy hop, b) lower edge advancing through a vacancy hop, and c) glide of the lower section of the core and vacancy diffusion.

surface is also shown. The data indicates that, around room temperature, the island hops about fifty times more rapidly than a single adatom, and that this difference increases even more as the temperature is lowered. This result demonstrates that large defects can actually be much more mobile than small ones, even at low temperatures. We were also able to explain, quantitatively, the curved temperature dependence of the hopping rate using a generalization of transition state theory with many intermediate states.

The fact that such a fast diffusion was unforeseen can easily be understood in light of the extremely complex mechanism by which it proceeds. Indeed, while the hopping process is cooperative, the island does not monolithically hop from one site to the other, but rather continually changes its conformation until a favorable sequence of such changes leads the island to the next site. Here, transitions are of two kinds: gliding (all or part of the core of the island coherently slides), and vacancy hopping along the edges of the island. Once again contrary to intuition, the hopping of these vacancies are the rate-limiting steps, while the rest of the island effortlessly follows the edges by gliding. The extreme complexity of the dynamics is shown in Fig. 3, where the network of states visited during a single Parallel Replica simulation of 6.5 μs at 175K is presented. In Fig. 3, each circle corresponds to a conformation, and two of them are joined by an arrow when a transition between them has been observed. Boxes contain conformations corresponding to perturbations around the same site, while the others correspond to intermediate conformations. The most efficient pathway for hopping is marked by colored arrows. A glimpse of some of the conformation changes occurring along this path is shown in Fig. 1.

In conclusion, we have shown that some metallic heteroepitaxial surfaces can evolve through the diffusion of very large islands containing many tens of atoms. We have also identified a novel mechanism involving vacancy diffusion and gliding that can confer mobility to such large defects. This work demonstrates that complex collective motions are often crucial in determining how crystalline surfaces behave and evolve.

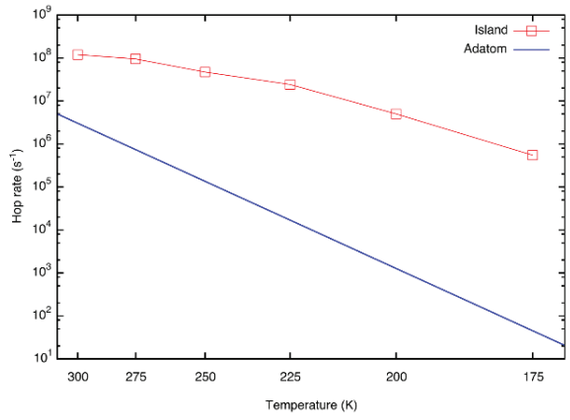

Fig. 2. Temperature dependence of the hopping rate of the island (red squares) and of a single adatom (thick blue line).

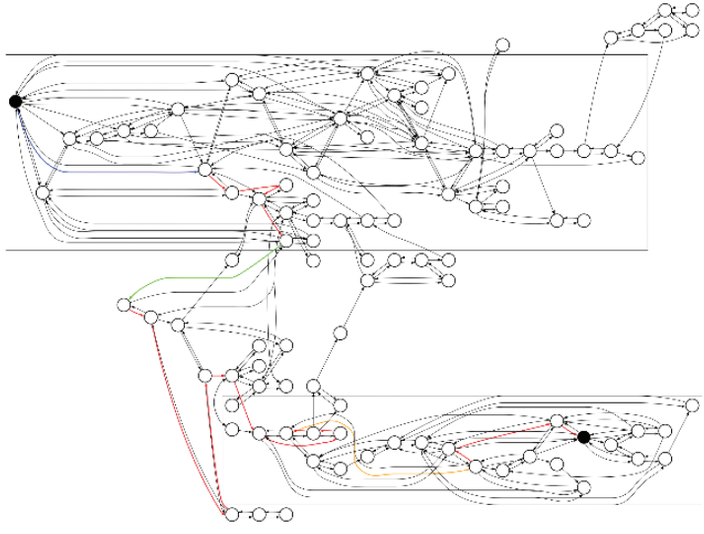

Fig. 3. Network of transitions observed during a Parallel Replica Simulation at 175K. Filled circles correspond to the conformations before and after the hop. Colored arrows correspond to transitions along the optimal pathway. The blue, green, and orange arrows correspond to transitions a), b), and c) in Fig. 1, respectively. See text for details.

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