Rapid Diffusion of Magic-Size Islands by Combined Glide and Vacancy Mechanism

O. U. Uche,[1] D. Perez,[2] A. F. Voter,[2] and J. C. Hamilton[1]
[1]*Sandia National Laboratories, Livermore, California, 94550, USA*
[2]*Los Alamos National Laboratory, Los Alamos, New Mexico, 87545, USA*
(Received 30 June 2008; published 22 July 2009)

Using molecular dynamics, nudged elastic band, and embedded atom methods, we show that certain 2D Ag islands undergo extremely rapid one-dimensional diffusion on Cu(001) surfaces. Indeed, below 300 K, hopping rates for "magic-size" islands are orders of magnitude faster than hopping rates for single Ag adatoms. This rapid diffusion requires both the $c(10 \times 2)$ hexagonally packed superstructure typical of Ag on Cu(001) and appropriate "magic sizes" for the islands. The novel highly cooperative diffusion mechanism presented here couples vacancy diffusion with simultaneous core glide.

DOI: 10.1103/PhysRevLett.103.046101 PACS numbers: 68.35.Fx, 68.55.−a

Surface diffusion is a fundamental physical phenomenon critical to the description of surface phase formation, epitaxial film growth, heterogeneous catalysis, and other surface processes. Various surface diffusion mechanisms have been described in the literature, comprising two general classes: single-atom jumping and cooperative processes involving simultaneous motion of two or more atoms. Historically, single-atom hopping dominated discussions of surface diffusion, thus surface diffusion of islands was thought to occur by adatom hopping via mechanisms such as edge running [1], terrace diffusion [2], and evaporation-condensation [2]. Our understanding of surface diffusion was changed dramatically by the discovery of cooperative diffusion in field ion microscopy experiments [3–5]. Subsequently, a number of processes have been observed which allow whole islands to diffuse with multiple island atoms moving collectively, including a simultaneous motion of all island atoms (island glide [6]) and dislocation mechanisms [7,8], involving nucleation and motion of misfit dislocations. Likewise, in dimer shear [9] and reptation [10] mechanisms, compact clusters undergo concerted shear motions as a means of translation. In this Letter, we describe a novel collective diffusion mechanism involving vacancy diffusion on two island edges coupled to simultaneous glide of the island core.

Here, we consider the system Ag on Cu(001). Previous theoretical work on this system [11] and the related Ag on Ni(001) system [12] has shown sliding of entire Ag overlayers but no diffusion of 40-atom islands or single chains of Ag atoms. Here, we reexamine finite island diffusion for the Ag-Cu system using the embedded atom method [13] with potentials from Mishin and co-workers [14,15]. We study hexagonally packed islands with the pseudohexagonal $c(10 \times 2)$ reconstruction typical of Ag on Cu(001) [16–18]. By virtue of the lattice mismatch ($[a_{\mathrm{Ag}} - a_{\mathrm{Cu}}]/a_{\mathrm{Ag}} = 11.7\%$), the monolayer of silver is row aligned on Cu(001) with 9 Ag atoms for every 10 Cu atoms. We will focus on hexagonal silver islands having 4, 5, 6, 7, 8, 9, and 10 atoms along each edge with a total of 37, 61, 91, 127, 169, 217, and 271 atoms, respectively. These islands exhibit a "magic-size" effect [8] in that the diffusion rate varies dramatically with size. In particular, the 169-atom and 217-atom islands diffuse much faster than the other island sizes and much faster than a single Ag atom. We will use the 169-atom island as a specific example of this effect.

We have used three complementary techniques, molecular dynamics (MD), parallel replica dynamics (PRD) [19], and nudged elastic band (NEB) [20]. MD provided a detailed atomistic view of every aspect of the diffusion process, allowing discovery of unexpected diffusion mechanisms and quantification of island hopping rates. PRD extended MD simulations to longer times and lower temperatures revealing lowest-barrier pathways for diffusion. The PRD simulations exploited the difference in time scale between fast core glide and slow vacancy diffusion, explicitly detecting only the vacancy diffusion transitions. NEB was used to calculate activation energies given detailed initial and final configurations from the MD and PRD runs [20].

Our starting configurations were a hexagonally packed $c(10 \times 2)$ Ag island placed atop four to five atomic layers of Cu(001) substrate with periodic boundary conditions in the in-plane directions. The bottom two layers of the Cu(001) substrate were frozen in place. A large number of quenched MD runs revealed that the stable ground state configurations for the 127-atom, 169-atom, 217-atom, and 271-atom islands are hexagonally packed and include vacancies in the two edges oriented along the $\{110\}$ direction. For these larger islands, vacancies are stable, accommodating the large size mismatch by separating the line of edge atoms into two shorter lines. For the smaller islands such vacancies are not stable.

The diffusion mechanism we report is driven by vacancy diffusion along the edges. For the 169-atom island the notation $n{:}8-n|m{:}8-m$ (n and m are integers) denotes the vacancy positions on two edges (see Fig. 1). First, the vacancies diffuse along the two edges, reach the end of the edge, and annihilate. Second, to complete a hop, new

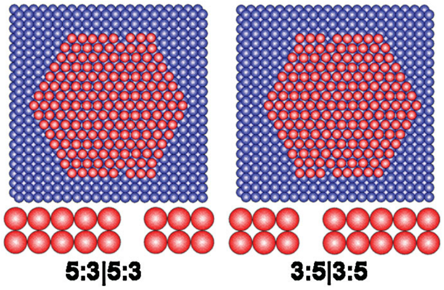

FIG. 1 (color). The two mirror symmetrical ground state configurations of the 169-atom island. We classify island states by the position of vacancies on the horizontal edges. The notation, n:8$-n$|m:8$-m$, means that the top edge has n atoms, a vacancy, and then 8$-n$ atoms, with a similar notation for the bottom edge. For configurations with no vacancy, the notation "8" is used.

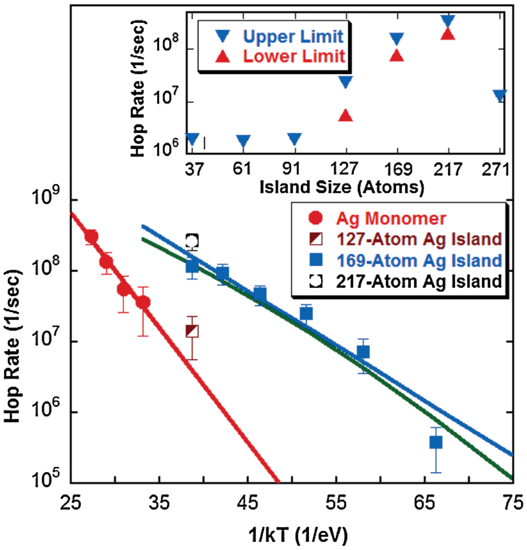

FIG. 2 (color). Temperature dependence of island hopping rates (limits from Poisson statistics at 95% confidence). At 300 K, the 169- and 217-atom islands diffuse much faster than the monomer or 127-atom island. At 300 K, the 37-, 61-, 91-, and 271-atom islands did not hop: only an upper rate bound is plotted in the inset. The Arrhenius fit for the 169-atom island (blue line) suggests an activation energy of 0.178 eV, in serious disagreement with our NEB calculation (Fig. 4) of 0.243 eV. The curved green line resolves the problem by having a slope equal to the temperature-dependent effective energy of activation (see text).

vacancies must nucleate at the other end of the edge and diffuse until the (translated) ground state reforms, denoted as 5:3|5:3 T [21]. The other island atoms maintain hexagonal packing and glide in concert with the vacancy diffusion on the edges. This diffusion process occurs exclusively along a single {110}-type direction along the long side of the $c(10 \times 2)$ reconstruction.

For the 169-atom Ag island, at temperatures $200 \leq T \leq 300$ K, MD simulations generally showed one or more island hops in 50 ns MD runs. Longer PRD simulations at 175 and 200 K also showed hopping. Figure 2 displays an Arrhenius plot of the hopping rates for the 169-atom island including 175 and 200 K PRD data. For comparison, hopping rates of 127- and 217-atom islands at 300 K and for a single Ag adatom at $350 \leq T \leq 425$ K are shown. Extrapolation of hopping rates to temperatures below room temperature [22] shows that the monomer diffusion is orders of magnitude slower than that of the 169- or 217-atom island [23]. The inset in Fig. 2 compares island diffusion rates at 300 K. For 37-, 61-, and 91-atom islands, there were no hops in ~2 μs simulation time and for the 271-atom island there were no hops in ~0.2 μs. For these islands the upper bound (95% confidence) is shown. This inset clearly demonstrates the magic-size effect. For fast diffusion, edge vacancies must form and annihilate easily; i.e., the vacancy formation energy may be negative or positive but must be small. Islands that are too small will have large positive edge vacancy formation energies; islands that are too large will have large negative edge vacancy formation energies.

We mention that for temperatures $T \geq 250$ K islands would occasionally depart from perfect hexagonal shapes. The "breakup" process involved atoms escaping from edge sites to become adatoms along the edge. Such islands became trapped, and no longer diffused by the vacancy-glide mechanism. Although such islands would often return to the perfect hexagonal shape and resume diffusion, we analyzed only simulation data prior to island breakup in order to accurately measure rates for vacancy-glide of the perfect hexagonal islands.

We now discuss the complex energy landscape of the 169-atom island. From all MD runs, we recorded atomic coordinates at 5 ps intervals and quenched using steepest descent energy minimization. The left side of Fig. 3 is a scatter plot of the center of mass (c.m.) coordinate (in the diffusion direction) versus the quenched energy. The stable ground states define the energy zero. We see that this system has a very large number of low-lying metastable states. The island energy exhibits translation symmetry with the 2.56 Å substrate periodicity. The ground states occur in pairs at $x_{\text{c.m.}} = 2.56p + 0.78(1 \pm 1)$ Å (p is an integer). A full hop of the island requires that p increase or decrease by one.

The right-hand portion of Fig. 3 shows the quenched c.m. coordinate as a function of time for the same MD run. To emphasize hops between stable ground states (and closely associated metastable states), we plot the c.m. coordinate (red square symbol) only for configurations having $0 < E_{\text{quenched}} < 0.04$ eV. The lines connecting these red points give us a map of the diffusion path between the low-lying states. We notice rapid diffusion between pairs of states with the same value of p (transitions between the states 5:3|5:3 and 3:5|3:5), and slower diffusion between states with different values of p (corresponding to transitions between 3:5|3:5 and 5:3|5:3 T). The rate-

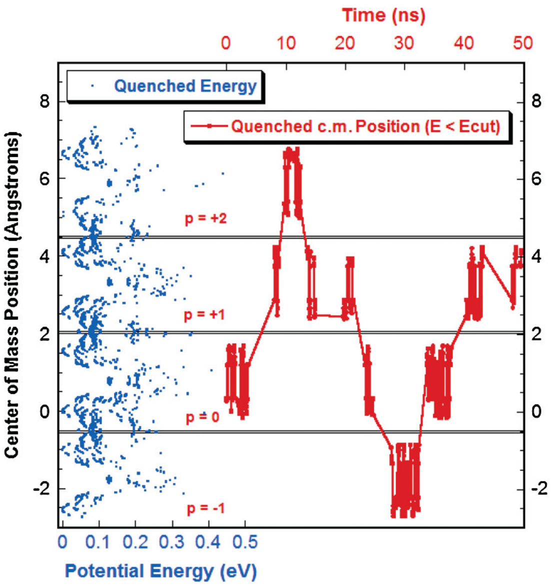

FIG. 3 (color). Center of mass coordinate for a 169-atom island MD run at 275 K. On the left-hand side is a scatter plot of quenched c.m. position versus potential energy. The system occupies a very large set of metastable states even at low temperatures. On the right-hand side is a plot of quenched c.m. coordinate versus time. The red points show the states in the immediate vicinity of the ground states ($E_{\text{quenched}} < 0.04$ eV). Transitions between red points are of two types: a rapid, glide-centric process which repeats frequently between 5:3|5:3 and 3:5|3:5 without completing a hop. The rate-limiting vacancy-assisted transitions (3:5|3:5 to 5:3|5:3 T) cross the double black horizontal lines, allowing a complete hop and determining the diffusion rate.

limiting transition between states with different values of p must occur to complete a hop. We counted hopping rates by counting crossings of the horizontal, black lines by the red trajectory.

Finally, we consider the activation energy for diffusion of the 169-atom island. It is possible to fit an Arrhenius expression (blue line in Fig. 2) to the hop rates; however, we will show that the inferred activation energy, $E_A = 0.178$ eV, is completely incorrect. In Fig. 4 the lowest observed energy diffusion pathway (extracted from a 175 K PRD run and refined using NEB) is plotted [23]. The highest transition state in this pathway yields $E_A = 0.243$ eV. An examination of the pathway reveals the two governing processes seen in Fig. 3: a rapid "mostly glide" process (5:3|5:3 to 3:5|3:5) and a slower "mostly vacancy" process (3:5|3:5 to 5:3|5:3 T). MD runs and NEB calculations both show that the rate-limiting process is annihilation of vacancies at one edge end and nucleation of vacancies at the other end. Two other observed 175 K pathways had energy barriers of 0.246 and 0.266 eV. While pathways slightly lower than 0.243 eV may exist, the barrier is much larger than 0.178 eV (from the Arrhenius fit).

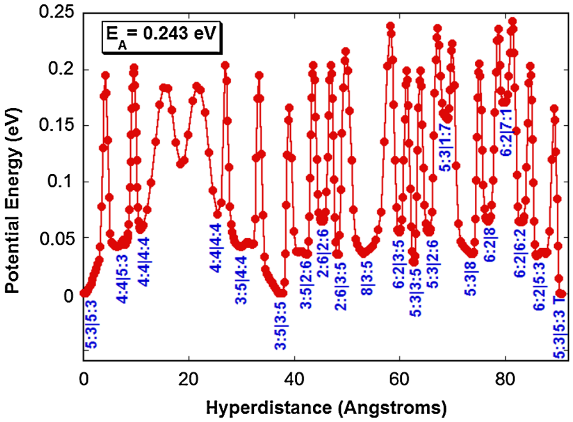

FIG. 4 (color online). Minimum energy path for surface diffusion of a 169-atom Ag hexagonal island based on 175 K PRD run and subsequent NEB analysis. States are labeled as in Fig. 1. The highest energy barrier is 0.243 eV. The intermediate state (3:5|3:5) is reached by extensive core glide with a few vacancy hops. The rate-limiting process (3:5|3:5 to 5:3|5:3 T) involves vacancy annihilation at one end and vacancy creation at the opposite end of the island edge.

The apparent discrepancy is resolved as follows: The NEB calculation gives the temperature-independent energy barrier between the ground state and the highest energy transition state along the diffusion pathway. However, the hopping rate is proportional to the rate at which the kinetic bottleneck is overcome (here 8|5:3 ⇒ 6:2|5:3) weighted by the probability that the initial state for this transition is occupied. Using the harmonic superposition approximation of the partition function, the effective activation energy for hopping is given by $E_A - \bar{E}(T)$, where $\bar{E}(T)$ is the average quenched energy of the system. For these temperatures $\bar{E}(T)$ can be approximated by the linear function, $\bar{E}(T) = b - \mathrm{m}/\mathrm{kT}$ with $b = 0.17$ eV and $m = 0.0021$ eV^2 (Fig. 5). Since the system has a large number of thermally populated low-lying states (inset in Fig. 5), this correction is significant. Upon integrating the slope of the Arrhenius plot, $E_A - \bar{E}(T)$, with respect to T, the hopping rate becomes $H_o \exp[-\beta E_A + \int_0^\beta \bar{E}(\beta')d\beta']$ where β is 1/kT and H_o is a free parameter to be determined by fitting. The resulting curved green line in Fig. 2 gives a good fit to the hopping rate. The failure of this Arrhenius plot to give the relevant barrier height sends a cautionary message to experimentalists.

In conclusion, we have shown that diffusion of hexagonal islands on a substrate with square symmetry can be remarkably fast. The energy barrier for this one-dimensional diffusion process cannot be determined from a standard Arrhenius analysis. We have proven the existence of magic-sized islands exhibiting fast diffusion at room temperature, contradicting the conclusion reached by Black *et al.* who reported that Ag islands on Cu(001) do not move in MD simulations at room temperature [11]. It appears that the islands they studied were not of the

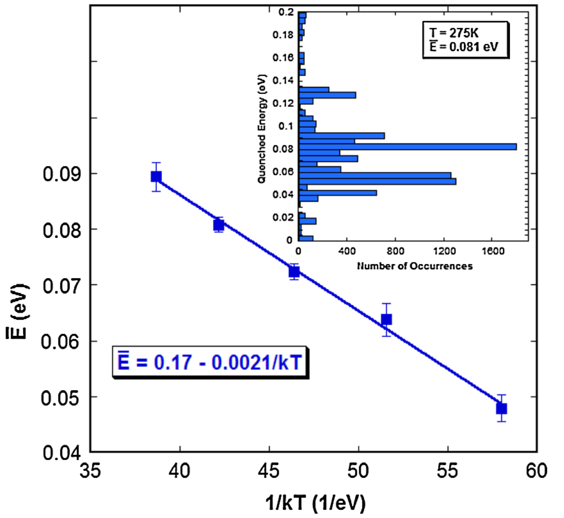

FIG. 5 (color online). The histogram inset shows the energy distribution of 169-atom island states quenched from a 275 K MD run. The mean energy $\bar{E}(T)$ of the quenched states is 0.081 eV. The plot shows $\bar{E}(T)$ vs 1/kT. The curved green line in the Arrhenius plot of Fig. 2 was fit using a temperature-dependent slope (effective activation energy), $\Delta E(T) = E_A - \bar{E}(T)$, with $E_A = 0.243$ eV from the NEB pathway in Fig. 4.

"magic size" required to show collective diffusion. We also note that Monte Carlo models of film growth, which generally allow only single atom hops, would neglect this complex cooperative mechanism.

Our results suggest a possible modification in the picture of film growth for Ag on Cu(001). The initial stages of film growth would occur via the deposition and diffusion of single atoms eventually forming critical nuclei which are immobile but continue to grow by addition of single adatoms. However, once these islands grow to a "magic size" they might diffuse rapidly and coalesce forming a network of connected islands. This process should be observable using STM at temperatures slightly below room temperature although it may require very particular deposition conditions to make magic-size islands. We hope that these theoretical results will inspire further experimental work to demonstrate this newly discovered diffusion mechanism and determine its effect on film growth in this and similar systems.

We gratefully acknowledge N. C. Bartelt for helpful discussions and NSF's Teragrid for providing computer resources. D. P. gratefully acknowledges Director's Funding at Los Alamos National Laboratory (LANL). This work was supported by the U.S. Department of Energy, Basic Energy Sciences, Division of Materials Science, under Contract No. DE-AC04-94AL85000 at Sandia National Laboratory and Contract No. DE-AC52-O6NA25396 at LANL. LANL is operated by Los Alamos National Security LLC, for the NNSA.

[1] A. F. Voter, Phys. Rev. B **34**, 6819 (1986).
[2] S. V. Khare, N. C. Bartelt, and T. L. Einstein, Phys. Rev. Lett. **75**, 2148 (1995).
[3] D. A. Reed and G. Ehrlich, Surf. Sci. **151**, 143 (1985).
[4] S. C. Wang and G. Ehrlich, Surf. Sci. **239**, 301 (1990).
[5] G. L. Kellogg and P. J. Feibelman, Phys. Rev. Lett. **64**, 3143 (1990).
[6] C.-L. Liu and J. B. Adams, Surf. Sci. **268**, 73 (1992).
[7] J. C. Hamilton, M. S. Daw, and S. M. Foiles, Phys. Rev. Lett. **74**, 2760 (1995).
[8] J. C. Hamilton, Phys. Rev. Lett. **77**, 885 (1996).
[9] Z.-P. Shi, Z. Zhang, A. K. Swan, and J. F. Wendelken, Phys. Rev. Lett. **76**, 4927 (1996).
[10] V. Chirita, E. P. Münger, J. E. Greene, and J. E. Sundgren, Thin Solid Films **370**, 179 (2000).
[11] J. E. Black, Z. Tian, and T. S. Rahman, Surf. Sci. **291**, 215 (1993).
[12] L. Yang, T. S. Rahman, and J. E. Black, Surf. Sci. **278**, 407 (1992).
[13] M. S. Daw and M. I. Baskes, Phys. Rev. B **29**, 6443 (1984).
[14] Y. Mishin, M. J. Mehl, D. A. Papaconstantopoulos, A. F. Voter, and J. D. Kress, Phys. Rev. B **63**, 224106 (2001).
[15] P. L. Williams, Y. Mishin, and J. C. Hamilton, Model. Simul. Mater. Sci. Eng. **14**, 817 (2006).
[16] P. W. Palmberg and T. N. Rhodin, J. Chem. Phys. **49**, 134 (1968).
[17] P. T. Sprunger, E. Lægsgaard, and F. Besenbacher, Phys. Rev. B **54**, 8163 (1996).
[18] A. Brodde, G. Wilhelmi, D. Badt, H. Wengelnik, and H. Neddermeyer, J. Vac. Sci. Technol. B **9**, 920 (1991).
[19] A. F. Voter, Phys. Rev. B **57**, R13 985 (1998).
[20] H. Jónsson, G. Mills, and K. W. Jacobsen, in *Classical and Quantum Dynamics in Condensed Phase Simulations*, edited by B. J. Berne, G. Cicotti, and D. F. Coker (World Scientific, Singapore, 1998).
[21] An analogy with diffusion of a single line of eight atoms illustrates this point. To translate a line of atoms by single vacancy hops, the line must pass through a sequence of configurations as follows: **5**:**3**, 6:2, 7:1, 8, 1:7, 2:6, **3**:**5**, 4:4, **5**:**3 T**.
[22] For the Ag monomer on Cu(001), exchange diffusion was not observed in any of our MD runs, consistent with our NEB calculation of a 1.08 eV barrier for exchange diffusion. This is much higher than the 0.40 eV barrier for adatom hop on the surface.
[23] See EPAPS Document No. E-PRLTAO-103-019932 for (a) an MD simulation of the diffusion of a Ag monomer and a 169-atom Ag island on the Cu(001) surface at 250 K and (b) an NEB movie of the lowest energy pathway for diffusion (see Fig. 4 of this Letter) of a 169-atom Ag island on a Cu(001) surface. For more information on EPAPS, see http://www.aip.org/pubservs/epaps.html.