Island Diffusion and Coarsening on Metal (100) Surfaces

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The diffusion and coarsening of two-dimensional homoepitaxial islands on Cu(100) and Ag(100) surfaces have been studied at room temperature with time-sequenced scanning tunneling microscopy. Quantitative analyses of the dependence of island diffusion coefficient D vs the island side length L, $D \propto L^{-\alpha}$, yield noninteger scaling exponents which are consistent with island coalescence. Moreover, the near absence of island decay shows that the island diffusion occurs via mass transport along the island periphery. [S0031-9007(97)04302-0]

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Diffusion of two-dimensional (2D) epitaxial islands on a substrate is an important subject in surface science and thin-film growth. Information about the elementary atomistic processes involved in thin-film growth may be extracted by simply studying the macroscopic island migration. A number of studies [1–5] have aimed at establishing a general scaling relation, $D \propto L^{-\alpha}$, between the diffusion coefficient D of a large island and the island side length L. Three dominant mechanisms have been proposed. If the island motion is caused by evaporation and condensation events as the island exchanges atoms randomly with the 2D (or 3D) gas (EC mechanism), then $\alpha = 1$. If the evaporation and condensation events are correlated, or equivalently, if the island motion is terrace-diffusion limited (TD mechanism), then $\alpha = 2$. If the island moves as a result of atom diffusion along the island periphery (PD mechanism), then $\alpha = 3$. These models predicting integer exponents describe, however, highly simplified or limiting cases. In fact, noninteger scaling behaviors or size-dependent scaling exponents have been observed in several Monte Carlo simulations [6–8] and detailed theoretical treatments [5,9].

Recently, the diffusion and coarsening of very large 2D islands (containing hundreds to thousands of atoms or vacancies) have been investigated with scanning tunneling microscopy (STM) [3,4,10–12], with quantitative measurements reported for Ag(100) [3,11] and Ag(111) [4,12]. For vacancy island diffusion on Ag(111), a value of $\alpha \approx 2$ was found and the TD mechanism was suggested to be dominant [4]. Nevertheless, as reported earlier [13], the evaporation rate of atoms from such island edges is nearly 3 orders of magnitude too small to account for the observed island diffusion coefficient. For adatom islands on Ag(100), a very weak (if any) dependence, $\alpha \approx 1$, was found, and the EC mechanism was suggested to be dominant [3]. The near integer exponents in both studies seem to support the simplified TD and EC models, and both experiments downplay possible contributions from the PD mechanism. This is questionable, because periphery diffusion is expected to be a faster atomistic process than evaporation of atoms [14].

In this Letter, we present the first known example where the periphery diffusion is, in fact, the main mechanism for island diffusion. We carry out a combined study of island diffusion, island coalescence, and island decay for two model systems, Ag on Ag(100) and Cu on Cu(100), at room temperature and in the submonolayer coverage regime. The rather small island decay rate shows that neither the TD nor EC mechanisms can be responsible for the observed island diffusion coefficients D. On the other hand, within the PD mechanism, the value of D yields a peripheral mass diffusion coefficient, D_s, that for Cu is comparable to the value obtained from a previous independent comprehensive step fluctuation measurement [15]. We also provide unambiguous experimental evidence of noninteger values of the scaling exponent, with $\alpha \sim 2.28$ for Ag and $\alpha \sim 2.49$ for Cu. Our results indicate that the usual assumption of structureless island periphery, which yields $\alpha = 3$, is inadequate. Within such an assumption, either jumps of single atomic spacing or a size-independent atomic edge diffusion coefficient is used. More physically, atoms can be trapped at the kink sites, but once released, they travel relatively fast along the straight segments of the island edges. Consequently, the diffusion coefficient of atoms moving along the periphery will depend on the detailed structure of the island edges, giving rise to a range of α values. One thus should not attempt to deduce the microscopic mechanisms for island diffusion solely based on the scaling exponent.

To visualize the dynamics of island diffusion and coarsening, images from time-lapse STM measurements were assembled into movies. From these movies, it is qualitatively evident that smaller islands move much faster than larger islands, and the disappearance of islands occurs exclusively via island collision. We performed three independent quantitative measurements. First, D vs L was measured following the procedure outlined by Morgenstern *et al.* [4]. This gives the exponent α. Second, the exponent β for the time evolution of coalescence-driven coarsening [6] was measured, i.e., $\overline{L} \propto t^{\beta}$, where $\overline{L}$ is the average island side length. Finally,

the decay rates of individual islands were analyzed. This gives an estimate of the evaporation rate of atoms from islands which will be shown to play an insignificant role in island diffusion in these systems.

Experimental data were acquired at room temperature (295–297 K) with a commercial (Omicron) STM housed in an ultrahigh vacuum chamber with a base pressure $<10^{-10}$ Torr. Cu and Ag substrates were prepared by sputtering and annealing, and submonolayer deposition of Cu and Ag were made at room temperature with an e^--beam evaporator. The deposition rates were adjusted to produce 2D compact islands with a coverage range of 0.08–0.14 monolayer (ML) and an island density range of $(4-9) \times 10^{-3}$ nm^{-2}. STM data acquisition was typically initiated 10–20 min after deposition to allow time for sample transfer and location of a terrace at least 200 nm wide. By collecting data from an area of 100×100 nm^2 on such a large terrace, the influence of preexisting steps is negligible. No sign of contamination was observed in either STM images or Auger spectroscopy. The STM images were obtained with a rate of 26–60 s/frame, a resolution of ~1 pixel/atom, a tunneling voltage (current) of ~0.5 V (~0.5 nA), and a thermal drift limited to ~(0.5–1.3) Å per minute.

Several STM movie series consisting of 730–1950 frames spanning 6–24 h have been assembled. Figure 1 shows the STM "snapshots" of Cu islands at the beginning and the end of a ~6 h series. The progression of images in the movies clearly shows motion and coalescence of the islands. Very little (if any) change in island size was observed between collisions for islands of sizes ranging from ~50 to ~730 atoms. When two islands of ~400 atoms in size touch each other, they rapidly reshape (within ~10 min) into a larger squarish island. As in previous reports [3], we also observed rounded corners of the compact islands. Qualitatively, Cu islands have rounder corners than Ag islands.

The STM images were analyzed as follows. First, islands in each frame were identified, their sizes and centers of mass calculated, and their traces mapped out. To calculate the diffusion coefficient of the islands, we measured the relative displacements, $\delta r = r_i - r_j$, between every pair of islands in the movie sequence, where r_i and r_j represent the centers of mass of the individual islands. The diffusion coefficient $D_{\{i,j\}}$ of an island pair then equals $\overline{[\delta r(t) - \delta r(0)]^2}/4t$. For better statistics, only pairs that can be followed for a minimum sequence of 50 frames were used to measure $D_{\{i,j\}}$, and $D_{\{i,j\}}$ was calculated by the weighted average of $\overline{[\delta x(t) - \delta x(0)]^2}/2t$ (or $\overline{[\delta y(t) - \delta y(0)]^2}/2t$) [16] where δx (δy) is the projection of δr parallel (perpendicular) to the STM scan direction. When both islands of an island pair are identical in size, the diffusion coefficient of each single island D is then $D_{\{i,j\}}/2$. Practically, island pairs with areas A_i and A_j (area A equals to L^2) within a reasonable tolerance $[\Delta_{\{i,j\}} = 2|A_i - A_j|/(A_i + A_j)]$ were chosen. Finally, a linear least square fit, $\log D = \log D_0 - \alpha \log L$, was used to extract α and D_0.
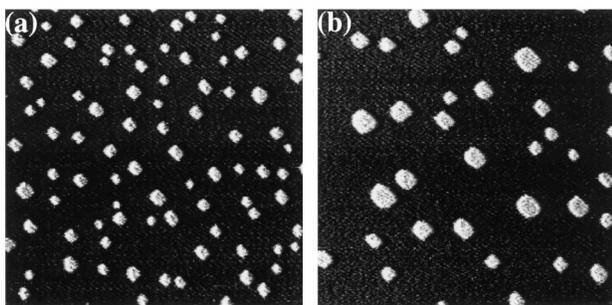
The main results are shown in Figs. 2 and 3. Figure 2(a) shows the results of α and D_0 for Cu, in which island pairs with sizes ranging from 80 to 440 atoms in ~730 images were used to obtain $\alpha = 2.49 \pm 0.09$ and $D_0 = (59.5 \pm 13.1)$ Å^2 s^{-1} for a reasonable choice of $\Delta_{\{i,j\}} = 15\%$. For the Ag data in Fig. 2(b), which covers island sizes from 60 to 870 atoms in ~1950 images, we found $\alpha = 2.28 \pm 0.10$ and $D_0 = (18.5 \pm 4.5)$ Å^2 s^{-1} with the same $\Delta_{\{i,j\}} = 15\%$. In both cases the exponent α varies slightly with the choice of $\Delta_{\{i,j\}}$. For $\Delta_{\{i,j\}}$ in the range of 5% to 15%, the values of α are within the error bars quoted
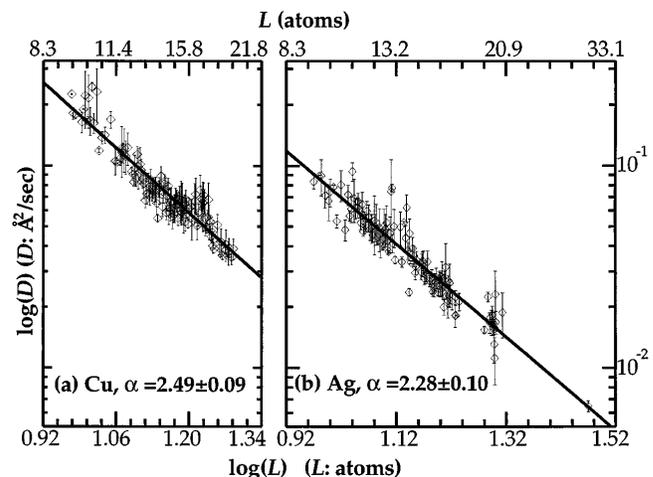
FIG. 2. Log-log plot of the island diffusion coefficient D as a function of island length L, where L^2 is the number of atoms in the island. (a) For Cu on Cu(100) ($\theta = 0.08$ ML, initial island density ~9×10^{-3} nm^{-2}). (b) For Ag on Ag(100) ($\theta = 0.14$ ML, initial island density ~9×10^{-3} nm^{-2}). Both plots of $\log D$ vs $\log L$ are reasonably fit by straight lines, indicating a scaling behavior $D \propto L^{-\alpha}$ with an effective exponent $\alpha = (2.49 \pm 0.09)$ for Cu and $\alpha = (2.28 \pm 0.10)$ for Ag. The error bars of individual data points only indicate the dispersion of measurements for distinct island pairs with the same size. Both (a) and (b) are plotted with a $\Delta_{\{i,j\}} = 15\%$ (see text).

FIG. 1. STM micrographs of a 100×100 nm^2 area of Cu on Cu(100) taken (a) several minutes after the completion of deposition and (b) 346 min later. Within ~6 h, islands have moved significantly and the island density has dropped 40% due to coalescence via island diffusion.
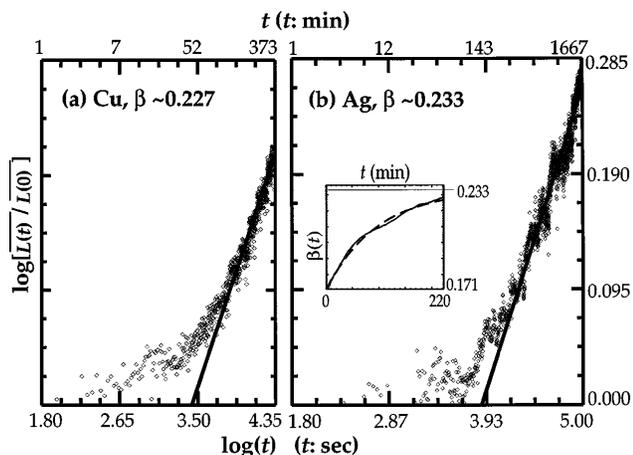
FIG. 3. Time evolution of the island coarsening via coalescence. (a) Cu on Cu(100). (b) Ag on Ag(100). After an initial "relaxation" time (on the order of 1 h), the average island size $\overline{L}$ grows approximately according to a power law, $\overline{L} \sim t^{\beta}$, where $\beta \sim 0.227$ for Cu and $\beta \sim 0.233$ for Ag at a late stage of the coarsening. Solid lines in (a) and (b) are fit to the above exponents, respectively. $\overline{L}$ is normalized with respect to the initial $\overline{L}$ at $t = 0$. The exponent β is obtained from its asymptotic approach, as shown in the inset in (b). See note [17] for more details.

above. We also found that after an initial "relaxation" time, $\overline{L}$ scales with time t as $\overline{L} \sim t^{\beta}$, with $\beta \sim 0.227$ for Cu [Fig. 3(a)] and $\beta \sim 0.233$ for Ag [Fig. 3(b)]. It has been shown theoretically that, at the late stage of coarsening and in the absence of Ostwald ripening, β is related to α by $\beta = 1/(\alpha + 2)$ [6]. It is easy to check that the independently measured values of α and β satisfy this relation reasonably well for both systems [17].

Is the deviation of α from an integer simply due to a competition between various mass transport channels? The answer is no. Specifically, we can show that neither the EC nor the TD mechanism can account for the observed island diffusion. This is done by examining the (adatom) island decay rate since it is related to the island diffusion coefficients D_{EC} (D_{TD}) for the EC (TD) mechanism [2,13]. Physically, both the atom detachment and attachment rates at the island boundary lead to island diffusion, whereas the difference between the rates leads to island decay or growth. A general expression for the island decay rate due to random detachment and attachment of adatoms has been obtained using various approaches [13,18]. Two limiting cases can be distinguished by the adsorption factor $\kappa = e^{-(\delta E_s/kT)}$ [13], where δE_s is the additional barrier (relative to the terrace diffusion barrier) required for an adatom to attach to the island edge. If κ is small (large), then the EC (TD) regime is reached. For the EC case, $\kappa \ll 1$, and

$$\frac{dA}{dt} \approx -2\pi D_a \rho_\infty \kappa R a \frac{\gamma a^2}{kTR},$$

$$\text{and} \quad D_{EC} = \frac{\kappa a^3 D_a \rho_\infty}{\pi R}, \tag{1a}$$

where A is the island area, D_a is the terrace diffusion coefficient of a single adatom, ρ_∞ is the equilibrium adatom concentration, a is the surface lattice constant, k is the Boltzmann constant, R is the island radius, and γ is the island edge line tension. Unlike Ref. [2], here the expression of D_{EC} in Eq. (1a) has specifically included κ in it. For the TD case, $\kappa \simeq 1$, and

$$\frac{dA}{dt} \approx -\frac{2\pi D_a \rho_\infty a^2}{\ln(l_c)} \frac{\gamma a^2}{kTR},$$

$$\text{and} \quad D_{TD} = \frac{a^4 D_a \rho_\infty}{\pi R^2}, \tag{1b}$$

where l_c (in units of R) specifies the distance over which the adatom concentration decays to ρ_∞. For simplicity, only the case of island decay is considered in Eqs. (1). It is important to note that, despite the apparent complexity of Eqs. (1), the only required parameters to estimate D_{EC} and D_{TD} from dA/dt (which we measure precisely) are γ and l_c.

In the case of Cu, we found that the islands hardly decay within 6 h ($|dA/dt| \leq 0.05$ atom/min). In the case of Ag, a slight Ostwald ripening occurs with a maximum decay rate of ~ 0.125 atom per minute. We then can estimate the upper bound of D_{EC} (or D_{TD}) from this decay rate via Eq. (1a) [or Eq. (1b)]. Using $\gamma \approx 105$ meV/a [19], $D_{EC} \approx 2.2 \times 10^{-5}$ Å^2 s^{-1} for $R/a = 10$ atoms. Assuming l_c varies between 1.01 to 10^2, $D_{TD} \approx 1.0 \times 10^{-4}$ to 2.1×10^{-7} Å^2 s^{-1}. These values of D_{EC} and D_{TD} are 2 to 5 orders of magnitude smaller than the experimental value of $D \approx (3-6) \times 10^{-2}$ Å^2 s^{-1} shown in Fig. 2. Hence, neither the EC nor the TD mechanism contributes significantly to the observed rates of island diffusion. Further supporting the results presented above, our measured magnitude of D for Cu is consistent with that from an independent and comprehensive study of step fluctuations on vicinal Cu(100) surfaces in which the mass transport is shown to be along step edges [15]. From Ref. [15], the diffusion coefficient of the mass transport along the kinked step edges, D_s, can be estimated to be ≈ 20 s^{-1} (in surface atomic units) for an island with estimated kink density ~ 0.1 at ~ 297 K. From the above D_s, we can estimate the island diffusion coefficient for the PD case using $D_{PD} = (D_s/\pi)R^{-3}$ (in surface atomic units) [1]. Setting $R = 10$, we find $D_{PD} \approx 0.04$ Å^2 s^{-1}, in good agreement with the observed $D \approx 0.06$ Å^2 s^{-1} shown in Fig. 2(a).

The observed noninteger scaling exponents by the PD mechanism may not be unexpected. The Langevin analysis developed by Khare et al. [9] shows that, even when the TD and EC mechanisms are explicitly forbidden, i.e., in a pure PD case, the "effective" exponent $\alpha(R)$ changes smoothly from 1 to 3 depending on a dimensionless quantity R/R_{st}. Specifically, $\alpha(R)$ changes from 1 at $R/R_{st} \sim 0.1$ to $\alpha \sim 3$ at $R/R_{st} \sim 10$. It is therefore likely that our systems lie in such a "crossover" regime, giving $\alpha \sim 2.3$ or 2.5. Since the detailed structure of

the island edges must affect the scaling behavior, we now conjecture upon the microscopic processes responsible for such a crossover. In general, there are many possible and distinct atomic processes along the island edge. The "rate-limiting" process causing the island diffusion must involve atoms detaching from kink sites since diffusion of atoms along straight island edges is significantly faster [8,14]. An atom detached from a kink site will either attach to a neighboring kink site or return to the original kink site. It is straightforward to apply a scaling analysis based on uncorrelated random atom transport between kinks [20]. We performed this analysis assuming a constant kink density, a random distribution of kinks, and that atoms detach from a kink site and attach to an adjacent kink site through a random walk [21]. Two interesting aspects can be clearly identified. First, $\alpha(R)$ changes continuously from 1 to 3 as R increases. In particular, $\alpha(R)$ closely matches the calculated form in Ref. [9] if their parameter R_{st} is interpreted as the average separation $\bar{l}$ between adjacent kinks. We also note that unlike the comments made in Ref. [9], it should be quite plausible to observe the crossover regime experimentally with a reasonable value of the angular kink separation ($\approx \bar{l}/R$). Second, $\alpha(R)$ increases with increased $R/\bar{l}$ for any given R. This appears consistent with our earlier observation that the Cu islands have rounder corners (i.e., smaller $\bar{l}$ for the same R) than the Ag islands, leading to $\alpha(Cu) > \alpha(Ag)$. It must be noted that the detailed behavior of the crossover may very well vary for specific systems. However, the above analysis, while highly simplified, provides a basic and reasonable physical picture for island diffusion via the PD mechanism.

Before closing, we note that our result for Ag contradicts the weak size dependence of D reported in the previous STM study by Wen et al. [3]. The discrepancy is most likely due to the much improved statistics in the present study [5]. On the other hand, the near absence of Ostwald ripening we observed for Ag is consistent with a more recent study by Wen et al. [11]. In our case the initial mean separation between the Ag island edges is ~ 64 Å for which Wen observed a coarsening mediated dominantly by island diffusion.

In summary, we have performed a comprehensive study of the diffusion, coarsening, and decay of submonolayer homoepitaxial islands on Cu(100) and Ag(100) at room temperature. A noninteger scaling law of the diffusion coefficient vs island size is clearly identified in both cases. The island diffusion is shown to occur via mass transport on the island periphery from the near absence of island decay. This conclusion is further supported by the quantitative consistency in the peripheral mass diffusion coefficient from independent island diffusion and step fluctuation measurements.

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[21] We assume the success probability for an atom to detach from a kink site and attach to an adjacent kink site through a random walk has a weak dependence on the kink-kink separation because of the presence of an island corner barrier.