Determination of Interlayer Diffusion Parameters for Ag/Ag(111)

K. R. Roos
Department of Physics, Bradley University, Peoria, Illinois 61625

M. C. Tringides*
Ames Laboratory and Department of Physics and Astronomy, Iowa State University, Ames, Iowa 50011
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It is well known that the Ag/Ag(111) epitaxial system grows three dimensionally because of the existence of a relatively high excess diffusion barrier, $\Delta E_s = 0.13$ eV, at the step edges. Several experimental methods have been developed to measure the step edge barrier in this system over a wide coverage range. The probability for an atom to move from a higher to a lower layer depends on both the barrier and the prefactor, so it is important to test whether the prefactors for hopping over a step, ν_s, and for hopping on a terrace, ν_t, are different. We present the results from several experiments on Ag/Ag(111) to conclude that $\nu_s/\nu_t = 10^{2.0\pm0.3}$.

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Surface diffusion measurements are performed as a function of different control variables (i.e., coverage, strain, step density) in an adsorbate system to determine how the usually applied parametrization of the results in Arrhenius form changes with the control variable. Two parameters are normally extracted in Arrhenius fits, the activation energy E which is a measure of the effective barrier the diffusing atom overcomes, and the prefactor D_0 which is commonly related to the vibrational frequency at the energy minimum of the initial site. This parametrization has been very successful in reconstructing the potential energy surface the adatom experiences. It has been observed that when both E and D_0 change systematically with the control variable there is a strong correlation in the way they change: As E increases it is found that there is correspondingly an increase in the value of D_0, the so-called "compensation" effect. In most cases there is a linear relation between E and $\ln D_0$. Recent experiments during epitaxial growth have shown that the barrier experienced by the adatom depends on the initial site from which it is hopping (whether it is a terrace site or a site at the step). Atoms hopping from sites at the step experience an additional barrier ΔE_s (which is usually positive). This barrier controls the amount of mass transported from higher to lower levels. In light of the previous discussion on the "compensation" effect, it is of great interest to measure the prefactors at the different sites to test if there is a corresponding increase of the prefactor as expected from the "compensation" effect.

The Ag/Ag(111) system is known [1–3] to have a relatively large step edge barrier which suppresses 2D growth at all temperatures studied. It has become a model homoepitaxial system for use in developing experimental methods [4–6] for measuring ΔE_s. A large step edge barrier can affect the selection of the slope during "mound" formation in epitaxy [7]. That the barriers to diffusion on a terrace and at a step edge are different can be attributed to a lower coordination experienced as atoms attempt to diffuse over a step separating different levels, although this generic argument cannot account for the large variation in ΔE_s values measured in different systems. It is generally assumed that the prefactors ν_t and ν_s for terrace diffusion and for interlayer diffusion, respectively, are the same; but, there is evidence suggesting different values for ν_t and ν_s in the Ag(111) system. In one scanning tunneling microscopy (STM) study [4] of Ag/Ag(111), a technique was proposed for relating ΔE_s to the fraction of first layer islands that have a second layer nucleated on top after depositing a fixed amount, based on the theory of Tersoff *et al.* [8]. Fits of the fraction of the islands with second layer occupation versus the average island size of the first layer island distribution have suggested that $\nu_s/\nu_t > 1$, but with large uncertainty because of the difficulty in quantifying the quality of the fit. In our earlier work [9] we have shown how this result can be confirmed from a new method that allows the separation of the two contributions to the interlayer probability (barrier and prefactor) in a unique way. In this Letter we present the results of complementary experiments with reflection high-energy electron diffraction (RHEED), and analyze additional aspects of the low temperature STM experiment to confirm not only the previous result, but to deduce a specific value, $\log(\nu_s/\nu_t) = 2.0 \pm 0.3$, for the ratio.

We first describe a series of Ag(111) homoepitaxial growth experiments we have performed at low temperature with time-dependent RHEED specular intensity to monitor submonolayer growth during deposition. The details of the Ag(111) preparation procedure and the experimental setup are found elsewhere [10]. The substrate is a well-annealed 40 ML film deposited on clean Si(111)-(7 × 7) according to similar preparation in the literature [11]. Shown in the inset of Fig. 1 is the peak intensity as a function of coverage for a typical growth experiment at low temperature. The hollow circles represent the typical intensity behavior during a deposit of 0.2 ML near an in-phase condition (with the normal component

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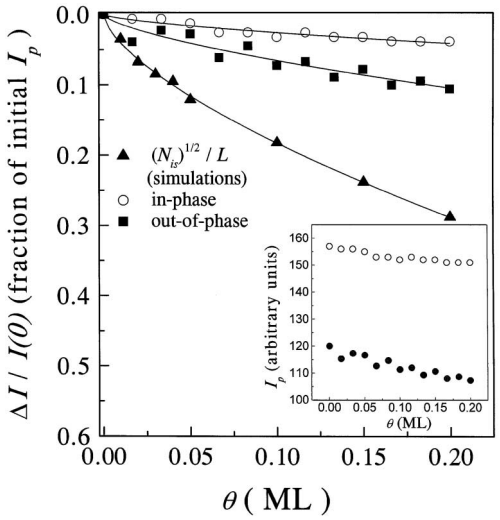

FIG. 1. RHEED peak intensity as a function of coverage for typical Ag/Ag(111) growth experiments at low temperature. The hollow circles represent the RHEED intensity behavior near an in-phase condition, and the solid circles represent the intensity behavior at an out-of-phase condition. The inset shows the raw data. The main plot shows the comparison of the typical fractional decrease $\Delta I/I(0)$ of the experimental peak intensity as a function of coverage with the analogous quantity $(N_{is})^{1/2}/L$ from the Monte Carlo simulations.

of momentum transfer $S_z = 2.6$ Å^{-1}), and solid circles represent the intensity behavior during the same deposit at an out-of-phase condition ($S_z = 3.9$ Å^{-1}). The surface temperature during the growth experiments shown in Fig. 1 was determined to lie in the range 150–170 K, based on a thermocouple near the Si sample and the measured change in the specular peak intensity of the prepared Ag(111) surface due to the known Debye-Waller factor. In this temperature range, the Ag adatom diffusion length is larger than the average Ag(111) terrace size. Ag adatoms diffusing on the surface have a high probability of sampling the terrace boundaries which are roughly 500 Å as measured from spot profile analysis [10]. This creates a unique growth regime, the "1-island regime," wherein the size of the few islands that nucleate and grow on the terraces during a low coverage deposit is influenced by the barrier ΔE_s to interlayer diffusion, as the islands compete with the terrace boundaries for atoms.

To understand the relation between the peak intensity decay and ΔE_s in our experiments we have developed a Monte Carlo simulation which realistically models submonolayer growth in the unique regime described above. A detailed description of the simulation model can be found elsewhere [6]. It was adapted in the current study so that the prefactor at the step edge can be extracted. In the simulations we measure the perimeter, or step density, of the islands that form in this growth regime. We assume that this essentially mimics the in-phase intensity decay behavior in the experiment since near an in-phase condition the intensity decay during the growth is predominantly due to diffuse scattering caused by the change of the step density on the surface. It is expected that the intensity decay will be greater at the out-of-phase condition, as observed in the inset of Fig. 1, since at an out-of-phase condition there is also kinematical sensitivity to lateral surface disorder. Figure 1 also compares the typical fractional decrease $\Delta I/I(0)$ of the experimental peak intensity with the analogous quantity $(N_{is})^{1/2}/L$, simulated under the same conditions (growth at 150 K corresponds to D/F, the ratio of diffusion to deposition rate, equal to 10^{11} in the simulations) as in the experiment. This comparison is fully justified in the low-coverage regime chosen since the fractional intensity change $\Delta I/I(0) \ll 1$ is sufficiently low to be fully due to the additional increase of the step density because of the nucleated islands. N_{is} is the number of atoms that join the few islands on the terrace, $(N_{is})^{1/2}$ is the total perimeter of the few islands, and L is the terrace length which determines the initial step density at the terrace boundary (i.e., the initial peak intensity). In the simulations we have assumed edge diffusion is extremely fast so islands have compact shapes which justifies the choice of the island perimeter as $(N_{is})^{1/2}$. The conclusions drawn in this paper are better justified for the case of noncompact islands as discussed later. Figure 2 shows typical simulation behavior for Ag(111) growth in the 1-island regime for coverage $\theta = 0.1$ ML, $D/F = 10^{11}$, and prefactor ratio of $\nu_s/\nu_t = 1$. The step edge barrier ΔE_s is 0 for the top panel, and $1.0E_t$ for the bottom panel. The extension of the ascending step can be seen on the top and left sides in each panel, and it clearly does not affect the initial step density at the terrace edges (atoms at the descending steps are not shown). It is clear that the island size, and thus the perimeter $(N_{is})^{1/2}$, is affected by the size of the step edge barrier at the descending boundaries. The perimeter of the terrace boundaries L remains essentially unchanged as ΔE_s changes.

In Fig. 1 it is clear that the in-phase decay is higher for all θ in the simulations than in the experiment by more than a factor of 5, which implies that the islands formed experimentally are smaller by at least a factor of 25 than those formed in the simulations. Thus, more adatoms made interlayer hops in the experiment than in the simulations. In the simulations we used $\Delta E_s = 0.13$ eV, as measured [4] for Ag(111) previously, and we assumed that the prefactors are the same. The only way to account for the enhanced interlayer diffusion observed in the experiment is to consider that the prefactor ν_s for the interlayer diffusion process is significantly greater than that, ν_t, for terrace diffusion. In the simulations, with the same value for ΔE_s, if the ratio ν_s/ν_t is increased to 100, then the simulation curve in Fig. 1 is raised to match the experimental curves. Clearly, the choice of $(N_{is})^{1/2}$ for the step density is an upper bound of the simulation curve shown in Fig. 1. If low edge diffusion is used, so that noncompact islands can form, the simulated step density would be more than $(N_{is})^{1/2}$, and the simulated curve in Fig. 1 would be even lower. This

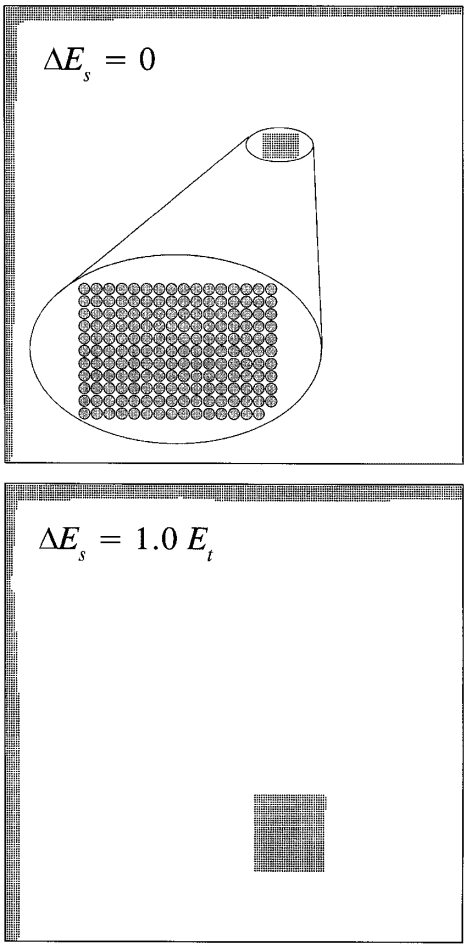

FIG. 2. The morphology of the "1-island regime" from kinetic Monte Carlo simulations of Ag(111) growth at a coverage of $\theta = 0.1$ ML for two different values of the step edge barrier ΔE_s. The simulations were performed on a 200×200 simulation cell with $D/F = 10^{11}$ [corresponding to growth on Ag/Ag(111) at 150 K]. The prefactor ratio ν_s/ν_t is 1.

would increase the discrepancy between the simulated and experimental step densities, and would thus make the difference in the prefactors even greater. It is important to stress that island shape is less significant for small coverages. It is less relevant in experiments performed with smaller terraces than in ones performed on macroscopic crystals.

Next we present, as further evidence that ν_s/ν_t is significantly greater than 1, a simplified approach to analyzing the data from the STM second layer nucleation experiment [4]. At the higher temperature $T = 130$ K where the sensitivity of the experiment to the value of ΔE_s is maximum (because the probability to hop to the lower level is larger) we see from the data displayed in Fig. 2 of Ref. [4] (which shows the fraction of islands with second layer occupation versus island size) that even for islands of radius 30 Å no nucleation on top of the islands is observed, or the fraction with second layer nucleation is zero. This indicates that for this rather large value of the initial island size, 30 Å, all the atoms deposited on top of the island reach the island edge and move from the top of the island to the lower level. We can estimate the fraction f of atoms landing on top of the islands which make successful interlayer hops during the second dose in the STM experiment. It should be the product of the number of edge interrogations, λ/d (with λ the diffusion length of a deposited atom and d the island diameter), and the hopping probability p:

$$f = \frac{\lambda p}{d} = \frac{(D_t \tau)^{1/2}}{d} \left(\frac{\nu_s}{\nu_t}\right) \exp\left(-\frac{\Delta E_s}{kT}\right). \qquad (1)$$

τ is the time between successive deposition events on top of a preexisting island during the second 0.1 ML dose and is expressed as $\tau = \frac{\Delta\theta}{F N_{\text{dep}}} = \frac{1}{FA}$, where $\Delta\theta = 0.1$ ML is the second dose, F is the deposition flux, A is the island size, and N_{dep} is the number of atoms which land on top of a typical preexisting island during the second dose.

We assume $\nu_s/\nu_t = 1$ and estimate f for the case where a second dose of 0.1 ML was deposited on preexisting islands of radius 30 Å at $T = 130$ K. $N_{\text{dep}} \approx 40$ atoms land on top of each one during the second dose. Using previously determined [4] values for ν_t and E_t, D_t is calculated to be $D_t \approx 3.5 \times 10^7$ hops/sec at $T = 130$ K. In the STM experiment, $F = 1.1 \times 10^{-3}$ ML/sec. If we use 130 meV [9] for ΔE_s, then Eq. (1) yields $f \approx 0.01$. This is in direct contradiction to what was observed in the STM study where *none* of the 30 Å islands displayed second layer nucleation on top, or $f = 1$. The only way to account for this discrepancy is that the ratio of the prefactors must be $\nu_s/\nu_t \approx 100$.

We next consider the effect of ΔE_s on the size of the denuded zone near the terrace boundaries in the Ag(111) system. One expects that as ΔE_s increases L_{desc}, the denuded zone near the descending steps, should decrease (and to a lesser degree L_{asc}, the denuded zone near the ascending steps, should also decrease). In the Monte Carlo simulations described above, we measure the size of the denuded zone adjacent to ascending and descending terrace boundaries as a function of the magnitude of ΔE_s. We define the size of the denuded zone to be the distance from the step to the nearest island. If $\Delta E_s = 0$ the denuded zones L_{asc} and L_{desc} near an ascending and a descending step, respectively, are the same; otherwise, for finite $\Delta E_s > 0$, L_{desc} is smaller than L_{asc}. In principle, this asymmetry can provide another way to estimate ΔE_s [12]. In the simulations an ensemble average of L_{asc} and L_{desc} is calculated for different growth configurations. We compare our simulation results to another STM study [13] of the Ag(111) system. The denuded zone observed on Ag(111) can be estimated by the "active" area wherein the steps compete for atoms with the few nucleated islands (i.e., close to the 1-island regime). To correct the deviation of the island density vs $1/T$ from the scaling relation, the active area is defined as the product, $\Lambda_{\text{cri}}\Lambda_{\text{emp}}$, where $\Lambda_{\text{emp}} (= 300$ Å) is an empirically determined [13] parameter, and Λ_{cri} is the largest substrate terrace width with no homogeneous nucleation,

measured with STM at different temperatures. We take $\Lambda_{emp}/\Lambda_{cri}$ to be the ratio of denuded zone length to terrace size at the temperature where capture of atoms by the steps is important. We estimate this ratio to be larger than 0.25 based on Fig. 2 of Ref. [13] wherein the terrace size (1200 Å) shown is larger than Λ_{cri} at that temperature. So the level 0.25 is a lower bound for the experimental ratio of denuded zone length to terrace size. We have carried out the simulations for $D/F \approx 10^{11}$, close to the 1-island regime, and in Fig. 3 we compare L_{desc}/L from the simulation to the experimental ratio 0.25 since Λ_{emp} is an effective average closer to L_{desc} than to L_{asc} [12]. The experimental ratio matches the simulations for $\Delta E_s \approx 0.5$ (with $\nu_s/\nu_t = 1$) which implies that for the canonical value of $\Delta E_s = 0.13$ eV, $\nu_s/\nu_t = 100$.

We have shown that the ratio of prefactors on Ag(111), for hopping over a step to hopping over a terrace, is greater than one. The conclusion was reached from several different experiments with different deposited Ag amounts, using different experimental probes which in a self-consistent way mutually support the conclusions reached in each experiment. Submonolayer growth experiments using RHEED follow the initial stages of nucleation from the specular intensity drop at fixed coverage as a function of substrate temperatures. The intensity drop, a measure of the fraction of atoms reflected by the barrier, is smaller than expected theoretically unless the ratio of prefactors becomes greater than one. STM experiments to measure second layer occupation on predeposited islands provide additional evidence about the larger prefactor at steps since the minimum size island where no second layer is observed is much larger (30 Å) than what is expected based on the large step edge barrier; in addition, the size of denuded zone measured in STM images is larger than what is expected from theoretical modeling. The increase of the prefactor at the step follows the corresponding increase of the barrier, another manifestation of the "compensation" effect commonly observed in diffusion studies, in the present study observed as a function of the location of the adsorption site, whether at steps or in the middle of terraces. On one hand, this strengthens the universality of the "compensation" effect and broadens the range of observations where it holds. But on the other hand, it poses serious theoretical challenges to provide a general explanation of this phenomenon.

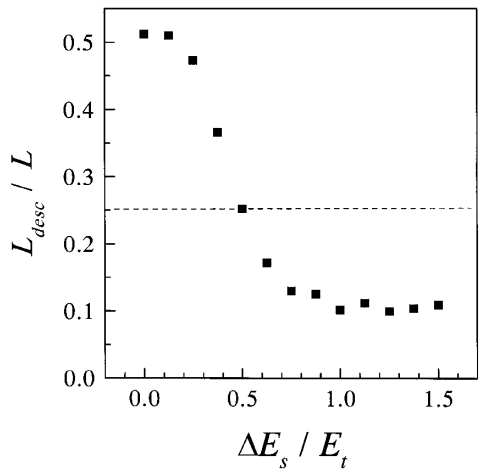

FIG. 3. The ratio of the denuded zone length L_{desc} near a descending terrace step to the terrace length measured in the simulations as a function of $\Delta E_s/E_t$ for $\nu_s/\nu_t = 1$. The dashed line represents the level 0.25 for the ratio estimated from the STM experiment [13]. The coverage is 0.1 ML and the ratio of deposition to flux rate is $D/F \approx 10^{11}$, close to the regime where steps compete with islands in capturing atoms. The value of the barrier $\Delta E_s/E_t = 0.5$ (for $\nu_s/\nu_t = 1$) is lower than the measured ratio $\Delta E_s/E_t = 1.3$, which implies $\nu_s/\nu_t = 100$.

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*Corresponding author.
Electronic address: tringides@ameslab.gov

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