Energetic Parameters for Atomic-Scale Processes on Ag(100)[†]

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Key energetic parameters that control growth and mass transport in clean Ag films and nanostructures on Ag(100) are compiled. These parameters have been derived from a number of different types of experiments, and from increasingly refined lattice-gas modeling, over several years. The modeling based upon these parameters appears to have good predictive capability in the temperature range 120−300 K.

1. Introduction

Understanding atomic transport, and associated collective rearrangements, at silver surfaces is important on several levels. First, certain properties of the surface of silver make it useful for key applications. For example, this is the surface of choice for surface-enhanced Raman scattering (SERS), and for catalysis in commercial ethylene epoxidation. Its surface dynamics may affect certain temporal phenomena that have been observed in these applications, such as the blinking associated with SERS from Ag nanoparticles,[1−4] and sintering of Ag catalyst particles. Second, dynamics on silver "turn on" at rather low temperature—many processes occur at significant rates even at room temperature. Hence, silver is a tractable prototype for investigation of the basic processes that occur at higher temperatures on higher melting point metals, such as Pt or Fe, where investigation is more difficult. Third, silver probably serves, in many respects, as a good representative of the coinage metals, which are gold, silver, and copper. Gold is the substrate of choice for self-assembled monolayers of alkanethiols, while copper is widely used in electronic devices. In both applications, surface rearrangements can be important.[5−7]

For some time, we have engaged in measurements and simulations of nonequilibrium nanostructures—both their formation and relaxation—in clean Ag thin films on Ag(100) in ultrahigh vacuum.[8] The main result has been the ability to develop tailored atomistic models for various aspects of silver surface dynamics that are sufficiently robust and comprehensive as to have *predictive* capability between 300 and 120 K.[9−12] We believe that such models could be used, for instance, to guide fabrication of films for SERS that have a particular desired morphology, or to predict the lifetimes of Ag nanostructures, in this range of temperature. Not only the models themselves, but also the parameters in these models, are significant. These parameters comprise a set of energies for detailed atomic-scale processes derived from comparing model predictions with experiment. They are useful because they can be compared with energetic parameters derived purely from theory, such as density-functional theory (DFT). Such a comparison provides a synergistic test of both the experiment and the theory.

Our understanding of the surface processes and energetics in Ag/Ag(100) has evolved with time. Hence, it may be useful to summarize the current view, and to make some comments about both strengths and weaknesses in derivations of the energetic parameters.

The approach[8] has been to measure surface structure, as a function of parameters including flux, temperature, time, and coverage, with scanning tunneling microscopy (STM) and high-resolution low-energy electron diffraction (HRLEED). The structural evolution can be modeled most effectively on the relevant experimental time and length scales using atomistic lattice-gas (LG) models for surface evolution, the behavior of which is analyzed using kinetic Monte Carlo (KMC) simulation. Two types of modeling strategies are possible: (i) tailored models focusing on the key physical processes described by a few free parameters (our approach);[9,13,14] or (ii) generic models including ∼10^3 rates or barriers for surface diffusion processes in all possible local environments (Voter approach).[15,16] Using the former, we have analyzed a sequence of increasingly complex experiments with a sequence of progressively refined models.

Note that a LG approach is inherently unable to identify the transition pathways in the kinetic processes, and so we do not postulate the exact mechanism by which an atom or group of atoms moves. For instance, terrace diffusion may occur via hopping or via place exchange. Diffusion over a step edge may occur again via hopping over the edge, or via a type of place exchange that can be called "push out". In a heteroepitaxial system, these processes would be distinguishable, because they would lead to different degrees of chemical intermixing.[17] In the homoepitaxial system we study here, the models are sensitive only to the initial and final state positions of the atom(s), not to the pathway linking the two. In all cases, we shall assume an Arrhenius form for the hop rates, $h = \nu \exp(-\beta E_{act})$, for various surface diffusion processes, where E_{act} is the activation barrier, ν is the attempt frequency, and β is $1/kT$.

2. Terrace Diffusion Barrier for Monomers, E_{d1}

During growth, atoms are deposited randomly on the surface with flux F (in monolayers (ML) per unit time), and then diffuse and aggregate into islands. At submonolayer coverages in homoepitaxial systems, an array of two-dimensional islands can form on terraces. The density of this array depends strongly on the degree of reversibility in the aggregation process, and the island shapes depend on edge diffusion processes. These, and other basic concepts in surface nucleation and growth, have been

reviewed and illustrated many times over. See, for example, refs 18−21. For Ag(100), this submonolayer regime is well-suited for determining the terrace diffusion barrier of single atoms.

In the simplest scenario, when pairs of atoms collide they irreversibly nucleate new islands, and atoms that collide with islands are irreversibly incorporated. Furthermore, the simplest assumption is that dimers, trimers, and larger islands are immobile (on the relevant time scale of island formation and growth). Then classic surface nucleation theory, based on mean-field rate equations, predicts that the average density of islands satisfies[18]

$$N_{isl} = C(h_1/F)^{-1/3} = C(F/\nu_1)^{1/3} \exp(\beta E_{d1}/3),$$
$$\text{for sufficiently large } h_1/F \quad (1)$$

In this equation, the rate for terrace diffusion by monomers is represented by $h_1 = \nu_1 \exp(-\beta E_{d1})$, and C is a constant that can be determined only approximately by rate-equation theories. Equation 1 is most useful for scaling analyses where the value of C is not needed and is accurate when h_1/F is sufficiently large, at least 10^5.[18,20,22] These restrictions can be circumvented by using an appropriate LG simulation, so simulation is preferable.

The value of the exponent, 1/3, reflects the stated assumptions about cluster mobility and stability. The exponent should differ from 1/3 if these simple assumptions are incorrect. Hence, one must check experimentally that the flux scaling assumed in eq 1 is valid, $N_{isl} \sim F^{1/3}$. Our experimental analysis for Ag/Ag-(100) at 300 K,[23] and more recently at 250 K,[24] finds flux scaling behavior consistent with the above picture. Therefore, we adopt that simple picture initially, although in the following section we suggest alternatives that would also be reasonable within the limitations of the data.

Analysis of Island Density at Fixed Temperature. For sufficiently low T in Ag/Ag(100), one expects irreversible formation of immobile islands which grow to have near square equilibrium like shapes due to efficient edge diffusion. Traditionally, data at a single temperature have not been used to analyze diffusivity since it requires knowledge of C in eq 1. However, one can readily perform simulations for a simple canonical square island model with the above features[13] to analyze experimental data for the island density (at a fixed low coverage of 0.1 ML, say) which depends only on the ratio h_1/F. Then, one simply adjusts h_1/F in the canonical LG model until matching the observed island density. Given the experimental F, and assuming $\nu_1 = 10^{13}$/s, one obtains $E_{d1} = 0.38$ eV.[23] We later revised this upward to 0.40 eV due to additional data.

In general, this approach suffers from the need to assume a value of ν_1. An early publication of $E_{d1} \approx 0.33$ eV for this system[25] was too low mainly because the assumed value of ν_1 was only 10^{12}/s.

Analysis of Island Densities at Variable Temperature. Temperature-dependent studies obviate the need for assuming values of either C or ν_1 in eq 1. For Ag/Ag(100), such studies were first performed using HRLEED and yielded $E_{d1} = 0.40 \pm 0.04$ eV from eq 1.[26] The diffraction data versus T could be fit with a LG model using $E_{d1} \approx 0.40$ eV and $\nu_1 = 3 \times 10^{13}$/s.[26] More recently, STM studies yielded $E_{d1} = 0.40$ eV, also from eq 1.[12] Actual values of N_{isl} versus T could be fit with a LG model using $E_{d1} \approx 0.40$ eV and $\nu_1 = 5 \times 10^{12}$/s.[12] The scatter in the STM data was significantly lower than in the HRLEED data, so we regard the STM-based values as more reliable.

Comparison with Other Available Information. The current best theoretical estimate of E_{d1} comes from DFT-GGA (generalized gradient approximation), and it is 0.45 ± 0.05 eV.[27,28] Within error, this agrees with experiment. It is also not far from earlier theoretical values, which came from effective medium (EM), embedded atom (EAM), and full-potential linear-muffin-tin orbital methods. The latter, for instance, yielded a value of 0.50 ± 0.03 eV,[29] which is somewhat above the range consistent with experiment.

The only other experimental data available for comparison comes from low energy ion scattering. Langelaar et al.[30] reported that Ag adatoms are immobile up to 160 K, at which temperature they become mobile enough to move to steps on Ag(100). Even though certain assumptions must be made in interpreting the data, the authors did report a value of 0.40 eV for the atomic diffusion barrier, consistent with our results.

As indicated in the Introduction, the above analysis does not determine whether the terrace diffusion mechanism is via conventional hopping or via place exchange. However, a high-level calculation has indicated that place exchange is clearly unfavorable in this system.[27,28]

3. Other Terrace Diffusion Processes

Other terrace diffusion mechanisms that should be considered include vacancy diffusion, and diffusion of dimers and other small clusters. These have been observed in some other metal-on-metal systems,[31−33] although not directly for Ag(100). Because the diffusion barrier in our analysis comes from measuring the island density that results from growth, let us consider whether and how those mechanisms could affect the island density.

The first process—vacancy diffusion—can be ruled out on physical grounds. During growth, there is a supersaturation of (deposited) Ag atoms. Some of these atoms will annihilate any vacancies. Hence, the role of vacancies in growth can be excluded. As noted in the Introduction, adatom diffusion via place exchange would not affect the nucleation analyses. The second process, dimer diffusion, cannot be ruled out. EAM calculations consistently suggest that the activation energy for dimer diffusion is not far above that of monomer diffusion.[34] The discussion below neglects diffusion of trimers. However, for metal (100) homoepitaxial systems, the barrier for trimer diffusion is likely to be comparable to that for dimer diffusion.[34] This could possibly lead to modification of the following analysis.

If the rate of dimer diffusion is significant, one has the modified scaling relationship.[35,36]

$$N_{isl} \sim (h_1 h_2/F^2)^{-1/5} \sim (F/\nu_{com})^{2/5} \exp\{\beta(E_{d1} + E_{d2})/5\} \quad (2)$$

where a common exponential, ν_{com}, is assumed for monomer and dimer diffusion, and $h_2 = \nu_{com} \exp(-\beta E_{d2})$ is the dimer hop rate.

A line with slope of 2/5 seems incompatible with our experimental data over the entire flux range, both at 250 K and at 300 K. However, if the system is in a crossover regime (see below), then the scaling exponent can be anywhere between 1/3 and 2/5. Furthermore, dimer diffusion could affect the flux scaling in a more subtle way, namely, by introducing slight nonlinearity. Hence, it is impossible to rule out *any* contribution from dimer diffusion (especially at 300 K), based on experimental flux scaling alone.

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A useful criterion for judging whether dimer mobility is significant is if the value of Y_{mob} exceeds ≈ 10, where this parameter is defined in terms of energetic quantities as[36]

$$Y_{mob} = (\nu_{com}/F) \exp\{-\beta(3E_{d2} - 2E_{d1})\} \qquad (3)$$

Since undoubtedly $E_{d2} \geq E_{d1}$, it follows that $3E_{d2} - 2E_{d1} > 0$, so one might expect a crossover from monomer to mixed monomer−dimer diffusion with increasing temperature. If this transition were to occur around 300 K for Ag(100), then for a typical experimental flux of $F = 0.06$ ML/s it follows that $3E_{d2} - 2E_d = 0.79$ eV. Thus, one obtains a reasonable[34] value of $E_{d2} = 0.53$ eV, assuming that $E_{d1} = 0.40$ eV. In other words, it is plausible that our data could be reinterpreted to include some contribution from dimer diffusion at 300 K. This correction could affect the values of E_{d1} derived from temperature-dependent data by increasing the diffusion barrier slightly (not more than about 0.05 eV). The change would be small, because the data for N_{isl} vs T span a range from about 180 to 300 K,[12,26] and over almost all of this range dimer diffusion would be negligible. This correction would, in turn, increase the predicted flux-scaling exponent, but the increase might be so slight that it would still be compatible with the data. A more definitive analysis of these issues requires more precise experimental data for N_{isl} versus F (at various T).

Finally, we comment briefly on current perspectives regarding monomer versus dimer diffusion in other homoepitaxial systems. First, data for submonolayer deposition of Cu on Cu(100) around 210−260 K was recently reinterpreted to argue for a significant influence of dimer mobility (but not mobility of trimers or larger clusters).[37] Second, detailed studies of submonolayer deposition of Ir on Ir(111) show a clear transition from a low-temperature regime of irreversible island formation ($i = 1$) with no significant dimer mobility to a higher temperature regime where $i = 1$ with significant dimer mobility (and then to a regime of reversible island formation at higher T).[38] The situation is less clear for other metal (111) homoepitaxial systems.

4. Dimer Bond Strength

In this discussion we will first assume that only monomers are mobile. With increasing temperature, island formation must eventually become reversible. Traditionally, one discusses this in terms of a critical size *above* which clusters are stable, i. We will use E_b to denote the binding energy of a cluster of two atoms.

The existence of well-defined critical size for $i > 1$ has been questioned,[39] but for metal (100) systems, one reasonably expects a transition directly from $i = 1$ (stable dimers) to $i = 3$ (stable tetramers) with increasing T.[23,40] Roughly speaking, scission of single bonds is inoperative in the former regime, but active in the latter (whereas double bond scission is inoperative for both). Experimental observations of N_{isl} versus T indicate that this transition occurs around 320 K for $F = 0.06$ ML/s.[25,41]

A useful criterion for the transition to reversible island formation is when Y_{rev} increases above ≈ 10,[23] where Y_{rev} is defined in terms of energetic quantities as[40]

$$Y_{rev} = (\nu_{com}/F) \exp\{-\beta(E_{d1} + 1.5E_b)\} \qquad (4)$$

From the transition temperature of 320 K and eq 4, we conclude that $E_b \approx 0.29$ eV (using $E_{d1} = 0.40$ eV and $\nu_{com} = 10^{13}$/s). Direct simulations fit the experimental data with a choice $E_b \approx 0.30$ eV, supporting this simple analysis.[23]

There is, however, a concern with these predictions. DFT-GGA calculations indicate a lower value for E_b of 0.22 eV.[42] One scenario for resolving this discrepancy is to consider the possibility that dimer mobility becomes significant at ~ 300 K and before reversibility at ~ 320 K. Then the definition of the parameter that predicts the transition to reversible island formation becomes[40,43]

$$Y_{rev}' = (\nu_{com}/F) \exp\{-\beta(3E_d - 2E_{d2} + 2.5E_b)\} \qquad (5)$$

Applying $Y_{rev}' \approx 10$, $E_{d1} = 0.40$ eV, $E_{d2} = 0.53$ eV, $F = 0.06$ ML/s, and $\nu_{com} = 10^{13}$/s in eq 5, we obtain $E_b \approx 0.26$ eV. This value is closer to the DFT-GGA estimate.

The main message here is that, for Ag/Ag(100), it is plausible that the transition to significant dimer mobility occurs before the transition to reversibility. This would slightly decrease the estimate of the dimer bond energy, E_b.

5. Ehrlich−Schwoebel (Step Edge) Barriers

During growth, as film coverage approaches and exceeds one monolayer, a significant fraction of atoms land on top of islands, and potentially form new islands in higher layers before the lower layers are completed. This feature is enhanced if downward interlayer diffusion is inhibited by an (additional) Ehrlich−Schweobel barrier at step edges. Spatial features in the growing film are rough, and in some cases are aptly described as mounds (multilayer stacks of islands). General scientific understanding of kinetic roughening has progressed very rapidly within the past 10 years. The current state is summarized well by Michely and Krug.[21]

Hence, the regime of multilayer roughening is well-suited for extracting the Ehrlich−Schwoebel (ES) barrier. We have found that, for simulations to match experimental data for Ag-(100), it is essential to introduce an ES barrier, E_{ES}, which is nonuniform. Specifically, along open, $\langle 100 \rangle$-type or highly kinked steps, the barrier $E_{ES\langle 100 \rangle} = 0$ is negligible, but along close-packed, $\langle 110 \rangle$-type steps, the barrier $E_{ES\langle 110 \rangle} > 0$ has a small but nonzero value. These results are qualitatively consistent with EAM results.[44,45]

Other noteworthy aspects of the simulations in this growth regime are the assumption of the same prefactor, $\nu = 10^{13}$/s, for interlayer diffusion as for terrace diffusion, and the incorporation of downward funneling[46] of atoms deposited at step edges to 4-fold hollow adsorption sites in lower layers. The results derived from two types of experiments using this analysis are given below.

Roughness of Multilayers below Room Temperature. Perhaps the most reliable, but demanding, assessment of $E_{ES\langle 110 \rangle}$ comes from analyzing the roughness of multilayer films versus deposition temperature. Experimentally, one finds that roughness increases as T decreases between 220 and 295 K,[11,47] in accord with the expectation that the ES barrier becomes progressively more influential. This trend, plus the actual value of the roughness, is very sensitive to $E_{ES\langle 110 \rangle}$, with the data for 25 ML being fit best by $E_{ES\langle 110 \rangle} = 0.07 \pm 0.01$ eV.[14]

Roughness of 1 ML at Room Temperature. Another estimation of $E_{ES\langle 110 \rangle}$ comes from depositing about 1 ML, and measuring the population of the second layer, θ_2. This population is sensitive to anisotropy in the ES barrier, and also to the magnitude of $E_{ES\langle 110 \rangle}$. Deposition at 300 K with $F = 0.06$ ML/s yields $\theta_2 \approx 0.06$ (with significant uncertainty), which corresponds to $E_{ES\langle 110 \rangle} = 0.07-0.10$ eV as determined by simulation using the multilayer growth model described above.[14]

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An early report of $E_{ES} = 0.03$ eV from this type of experiment was based upon the incorrect assumption of a single, isotropic ES barrier,[41] so this value should be regarded as a weighted average of $E_{ES\langle100\rangle}$ and $E_{ES\langle110\rangle}$.

6. Step Edge Diffusion Processes: Kink Rounding Barrier

Shape Transition in Two-Dimensional Islands. As noted above, efficient edge diffusion in Ag/Ag(100) produces nearly square-shaped, compact islands. The two key edge diffusion processes controlling island growth shapes are diffusion along the straight portion of the step and rounding of (single atom high) kink sites. Of these two step edge diffusion processes, kink rounding is the slowest and is hence most crucial for determining island shapes during growth.

Kink rounding is critical because, for islands to have compact shapes, the time for an atom on an island edge to round a kink and reach a doubly coordinated step site must be less than the time between arrival of aggregating atoms. Otherwise, the aggregating atoms will form new, incomplete rows along the edge. Equating these two times gives a criterion for the onset of deviation from compact shapes—the so-called island shape instability.[14,48−52] Our STM observations indicate that submonolayer island shapes become irregular around 175 K at $F = 0.006$ ML/s.[12] Using the specific criterion outlined in ref 52 then yields the rather crude estimate that $E_{kr} = 0.45$ eV.[12]

Roughness of Multilayers in the Regime of Reentrant Smoothness. As T falls below $\sim$230 K, the roughness of multilayer films of some prescribed thickness (e.g., a few dozen monolayers) starts to diminish; i.e., there is reentrant smoothness.[11,47] This effect is due at least in part to the enhanced influence of downward funneling, due to the higher density of step edges at lower T. However, while a model with efficient periphery diffusion and downward funneling does indeed produce this reentrant growth, it overestimates the roughness below 230 K. The resolution to this discrepancy comes from the recognition that kink rounding is increasingly inhibited in this temperature range, causing islands to become more irregular. This increases the relative population of kinked step edges, and thus lowers the overall or effective ES barrier, which also makes the film smoother. Indeed, modification of the model to include a nonzero kink rounding barrier reveals that film roughness below 220 K is quite sensitive to E_{kr}. The best fit to experimental data is achieved with the choice $E_{kr} = 0.41$ eV.[9,50]

7. Other Step Edge Processes and Information

$\langle110\rangle$-**Type Edge Diffusion.** DFT-GGA studies reveal that the barrier for diffusion along the straight, close-packed, $\langle110\rangle$-type edges is $E_e \approx 0.25$ eV,[28] so this process is very efficient. The total barrier for kink rounding can then be regarded as this barrier, plus an additional energy, δ, which is the one-dimensional analogue of the Ehrlich−Schwoebel barrier. In other words, $E_{kr} = E_e + \delta$. The values given above for $E_{kr} = 0.41−0.45$ eV lead to $\delta = 0.16−0.20$ eV.

Postdeposition Relaxation. Studies of relaxation (time-dependent reshaping, or coarsening) of Ag/Ag(100) nanostructures have also yielded energy parameters relevant to step edge diffusion and binding. However, these studies do not yield single parameters, but yield rather a *sum* of parameters.

One class of relaxation processes is that in which submonolayer islands later diffuse and collide with each other and with step edges. These far-from-equilibrium nanostructures then relax to their equilibrium forms. Assuming that this process is governed by a mechanism known as periphery diffusion (PD),

analysis of the characteristic relaxation time (or rate) provides information on the overall or effective PD barrier:[65]

$$E_{PD} = E_{kr} + E_b = E_e + \delta + E_b \qquad (6)$$

One caveat is that this expression applies only to relaxation of nonconvex shapes, and only within the framework of a nearest neighbor interaction picture.[65] Here, the bond strength, E_b, (cf. section 4) equals twice the kink creation energy, and E_{PD} gives the barrier for "core breakup", which is the reverse process of kink rounding by an isolated step edge atom. We note that a different barrier describes the characteristic time for fluctuations at an equilibrium step edge[53] and for the relaxation of convex faceted shapes,[65] where distinct physics dominates behavior.

Our first analyses of relaxation data for small nanostructures at a single temperature of 295 K produced an estimate of $E_{PD} = 0.75$ eV (assuming prefactors of 10^{12}/s).[54] Two later analyses suggested that this estimate was a little too high. First, we obtained data for the rate of relaxation of the height of a 10 × 10 atom square at a $\langle110\rangle$-type step edge at 250 K of 0.4 Å/s, which could then be compared against the rate of 20 Å/s for the same sized protrusion at 298 K. This comparison produced a crude estimate of $E_{PD} = 0.7 \pm 0.1$ eV.[55] Second, the time scale of PD-mediated evolution and pinchoff of large wormlike vacancies on Ag(100) was successfully recovered from continuum modeling with $E_{PD} = 0.68$ eV.[56] We regard this as the better of the two values.

We can check whether things are internally consistent by seeing whether eq 6 holds true after substituting the best values from the various experiments and analyses described thus far (in eV):

$$E_{PD} = 0.68 \qquad E_{kr} + E_b = 0.41 + 0.30 = 0.71$$

The numbers are consistent to within 0.03 eV. Recall that the last value, 0.30 eV for E_b, is an upper limit in light of potential dimer diffusion. The value of 0.26 calculated in section 3 is probably more appropriate, and this would make the numbers consistent to within 0.01 eV.

8. Discussion

It is instructive to compare behavior for Ag/Ag(100) with that for Cu/Cu(100). Durr et al. used HRLEED to measure the temperature dependence of the island separation in submonolayer deposition of Cu on Cu(100).[57] They derived values of E_{d1} and E_b[23] that were both disconcertingly low—lower than the values for Ag/Ag(100), despite the higher cohesive energy of Cu relative to Ag.[58] Furthermore, Durr et al. reported a transition to reversible nucleation well below the transition temperature of Ag/Ag(100), again unexpected based on cohesive energies. However, recently the Cu/Cu(100) experiments were reanalyzed, leading to an increase in both the energy values and the transition temperature.[37] The reanalysis incorporated dimer diffusion with a barrier similar to that of monomer diffusion.[37] This indicates that major aspects of the relative behavior of (100) metal surfaces scale according to cohesive energy.[58]

Throughout this article, we have tried to point out the key aspects of our modeling. One that has been mentioned only briefly is the fact that only Ising-like nearest-neighbor interactions are taken into account; next-nearest-neighbor interactions are assumed to be weak. This is reasonable, based on detailed examination of EAM results,[16,34] for the processes we consider. Einstein et al. have shown that sometimes the weaker, longer range interactions can be important, particularly in consideration

of equilibrium phenomena such as island shapes.[59] In contrast, our studies all deal with situations where the surface is far from equilibrium, where one would expect the finer details of the interactions to be less important.

Another caveat regards the temperature range over which the multilayer growth modeling is applicable. For multilayer growth below 120 K, there is a breakdown of downward funneling which can lead to bulk vacancies incorporated during growth,[11] although this is offset by the emergence of multiple interlayer diffusion processes with low energy barriers. For these reasons, the multilayer model described above does not apply below 120 K. A different multilayer growth model, tailored to incorporate these features in the absence of terrace diffusion, was developed and applied to growth below 120 K.[60] For postdeposition coarsening or relaxation above room temperature, one might expect terrace diffusion of adatoms or vacancies to become important, as it does on Cu(100). This may set an upper limit on validity of our modeling of these processes based on periphery diffusion.

Despite the cautionary notes above, the modeling has achieved some strong successes. First, it has proven adequate to describe data for submonolayer island formation at low coverages over a broad range of temperatures.[12] Although the modeling incorporated only one adjustable parameter, it was able to recover both classic scaling behavior at room temperature and more complicated behavior at very low temperature, where nucleation continues to occur even after deposition stops.

A second reinforcement, obtained with a relatively crude multilayer growth modeling incorporating a uniform ES barrier and square islands, was in the prediction of reentrant smooth growth in this system.[10,61] Five years after the prediction was made, it was verified by experiment for Ag/Ag(100).[11,47] Later, it was necessary to refine the model[14] to account for all the structural details within a full set of experimental data, but still, its major original prediction had proven correct.

A third success came from the refined multilayer growth model with a nonuniform ES barrier. The standard view had been that homoepitaxy of Ag on Ag(100) around room temperature is the prototype of smooth quasi-layer-by-layer growth,[62] in contrast to the rough, wedding-cake-like mound structures formed for Ag on Ag(111).[63] The difference had been rationalized in terms of a qualitatively large ES barrier for Ag/Ag(111) of ~0.13 eV versus a small ES barrier for Ag/Ag-(100), estimated at ~0 eV from DFT-GGA.[27,28] However, we showed that there is a nonzero ES barrier of ~0.07 eV on the close-packed steps of Ag/Ag(100). Furthermore, we challenged the fundamental view that growth on Ag(100) is smooth under typical conditions. Our simulations of film growth at 300 K did reveal an initial mound formation regime of fairly smooth growth, but this is followed by an extensive mound steepening regime, up to at least 1500 ML, wherein growth is very rough.[9]

A fourth achievement relates to postdeposition relaxation of two-dimensional step edge nanostructures.[64] Experiments revealed that the relaxation time scaled like the third power of the feature size, rather than the fourth power expected from classic Mullins theory. Our simulations incorporating a substantial kink ES barrier recovered the unconventional behavior and showed definitively that it was related to the presence of a significant nonzero kink ES barrier.[65]

Together, these positive results provide the basis for our assertion that the modeling incorporates the key mechanistic processes (with the possible exception of dimer vs monomer diffusion during growth), that the energetic parameters are

TABLE 1: Experimental Values of Energetic Quantities Derived for Ag(100) from Our Work[a]

quantity	value (eV)	preexponential	technique	data analysis notes	ref
single-atom terrace diffusion barrier, E_{dl}	0.40	assumed $\nu_1 = 10^{13}$ s^{-1}	STM: analysis of island density at fixed temperature	E_{dl} could be higher by as much as 0.05 eV if dimer mobility is significant. (See text.)	b
	0.40 ± 0.04	determined $\nu_1 = 3 \times 10^{13}$ s^{-1}	HRLEED: analysis of island densities at variable temperature		26
	0.40*	determined* $\nu_1 = 5 \times 10^{12}$ s^{-1}	STM: analysis of island densities at variable temperature		12
Ag–Ag dimer dissociation energy on a (100) terrace, E_b	0.30	assumed equal to ν_{dl}	STM: temperature at which N_{isl} vs T becomes nonlinear	E_b could be lower if dimer mobility is significant. (See text.)	23
ES barrier to cross a ⟨110⟩-type step, $E_{ES\langle110\rangle}$	0.07 ± 0.01*	assumed equal to $\nu_1 = 10^{13}$ s^{-1}	STM: roughness of multilayers below room temperature		14
	0.07–0.10		STM: roughness of 1 ML at room temperature		14
kink or corner rounding barrier for an atom on a ⟨110⟩-type island edge, E_{kr}	0.45	assumed equal to ν for straight ⟨110⟩-type edge diffusion	STM: temperature of shape transition in two-dimensional islands		12
	0.41*	neither assumed nor derived	STM: roughness of multilayers in the regime of reentrant smoothness		9, 50
sum of barriers $E_{kr} + E_b$	0.7 ± 0.1	assumed $\nu_{kr} = 3 \times 10^{12}$ s^{-1}	STM: postdeposition relaxation		55
	0.68*				56

[a] In cases where multiple types of experiments and analyses yielded a single parameter, an asterisk (*) denotes the value we deem most reliable. [b] Refined from original publication in ref 23. See text.

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