Energetic and Entropic Contributions to Surface Diffusion and Epitaxial Growth

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For Pd/Pd(111) an exceptionally high barrier (350 meV) for surface self-diffusion and a negative additional energy $\Delta E = -53$ meV for step-down diffusion are measured. Both findings agree with the proposed role of free-electron-like surface states. Despite the negative value of ΔE layer-by-layer growth is not observed. This is related to the low preexponential factor for step-down diffusion. Preadsorption of oxygen increases ΔE but flattens the films. Again this is due to the prefactors for diffusion. The present results demonstrate the importance of entropic effects for diffusion and growth.

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Controlling the morphology of epitaxially grown films is of great technological interest. Whereas in some applications (e.g., production of magnetic storage devices) flat films are required, rough films with well-defined cluster sizes and densities are desired in others (e.g., heterogeneous catalysis). Proper choice of the deposition flux F and the substrate temperature T in relation to the material parameters of the film/substrate combination allows one to control the film morphology within certain limits. The microscopic parameters most important in this respect are the hopping rates $h = \nu \exp(-E/kT)$ and $h_S = \nu_S \exp[-(E + \Delta E)/kT]$ for diffusion of the deposited adatoms on the flat surface and over downward steps, respectively. The ratio of the former quantity to the deposition flux F determines the island (= cluster) density n_x, which scales as

$$n_x = \eta(\Theta)\left(\frac{F}{h}\right)^{1/3} \tag{1}$$

in the case of irreversible island aggregation [1,2]. The factor η depends on the coverage Θ and is of order unity [3]. The rate h_S for "hopping" of adatoms over downward steps (in combination with h and F as discussed further below) controls the interlayer mass transport and hence the film roughness. Thus, a knowledge of the energy barriers E and ΔE as well as the prefactors ν and ν_S is highly desirable. This has stimulated considerable theoretical and experimental work on energy barriers [4]. The prefactors, in contrast, are often assumed to have a universal value of $\approx 10^{13}$ s^{-1}, independent of the material and the microscopic diffusion mechanism. In particular, in kinetic Monte Carlo simulations of epitaxial growth this assumption is usually made, although previous experiments already indicate that this is not always true [5].

In the present paper the diffusion of Pd on clean and oxygen-covered Pd(111) is investigated by scanning tunneling microscopy (STM). Barriers and prefactors for diffusion are deduced from nucleation and growth experiments. The Pd/Pd(111) system is of particular interest with respect to the recent proposal [6] that occupied free-electron-like surface states lower the diffusion barrier E on the flat surface and increase the additional step-edge barrier ΔE [Ehrlich-Schwoebel (ES) barrier]. Among the fcc transition and noble metals, Pd is the only metal which does not support such an occupied surface state on the (111) surface [6,7]. Accordingly a high value of E and a low value of ΔE were predicted for Pd(111). The present experiments show that this is indeed the case. Furthermore, the present analysis reveals that the prefactors, too, strongly influence the film roughness. In the formalism of transition state theory [8] ν (and similarly ν_S) is given as $\nu \approx N\,kT/h_p \exp(1 + S/k)$. Here h_P denotes the Planck constant, N is the number of jump-equivalent neighbor sites, and S is the difference of the entropy between the transition state at the saddle point of the potential energy surface and the initial state in the equilibrium adsorption site. A strong influence of the prefactors therefore implies significant entropic contributions to surface diffusion and to the growth of thin films.

The experiments were carried out in a UHV system (base pressure $<5 \times 10^{-11}$ mbar) with a variable-temperature STM. Pd was deposited with a rate of 4×10^{-3} ML/s by electron-beam bombardment of Pd wires (purity 99.998%). Pd ions created by the electron bombardment were electrostatically deflected to avoid their impingement on the surface.

Figures 1(a) and 1(b) show STM images of 0.08 ML Pd deposited at 210 and 420 K onto the Pd(111) surface [9]. The island densities obtained from such images are depicted in the Arrhenius diagram [Fig. 1(c)] for deposition temperatures between 210 and 420 K. On the clean Pd surface the data points follow a straight line up to a temperature of 375 K. The clear break in slope at 375 K indicates a change in the nucleation mechanism. Below 375 K nucleation is dominated by the mobility of single atoms, while clusters—once formed—are stable and do not decay (critical island size $i = 1$). This is evident from the scaled island-size distributions which are plotted in Fig. 1(d) for deposition temperatures of 250 and 300 K. The data disagree with the distributions expected, if small clusters—dimers ($i = 2$) or trimers ($i = 3$)—can decay, but follow the theoretical curve for irreversible island

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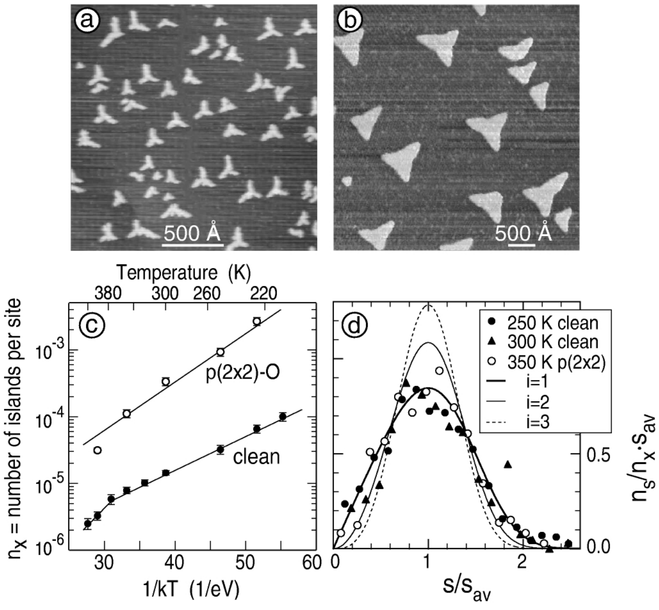

FIG. 1. STM images of 0.08 ML Pd/Pd(111) deposited at (a) 210 K and (b) 420 K. (c) Semilog plot of island density n_x versus inverse temperature for deposition onto the clean and $p(2 \times 2)$-oxygen precovered Pd(111) surface. (d) Scaled island-size distributions in comparison with theoretical results for critical island sizes $i = 1$, 2, and 3 [29]. n_s denotes the density of islands of size s and s_{av} the average island size.

aggregation ($i = 1$). Hence, Eq. (1) applies, and the barrier and prefactor for surface diffusion can be obtained from a fit to the low-temperature data ($T \leq 375$ K). Using $\eta(0.08 \text{ ML}) \approx 0.38$ [1,2] this yields $E = 350 \pm 40$ meV and $\nu = 6 \times 10^{16\pm0.6}$ s^{-1}.

The barrier $E = 350$ meV for self-diffusion on Pd(111) is the highest value observed so far on a clean fcc (111) metal surface [9]. This finding supports the proposal that occupied free-electron-like surface states lower the surface diffusion barrier, while on Pd(111)—where the surface state is completely unoccupied—the barrier is relatively high. The high value of the prefactor $\nu = 6 \times 10^{16}$ s^{-1} is quite puzzling, at least at first sight. However, as discussed in more detail elsewhere [9], it is in accordance with the Meyer-Neldel compensation law, which predicts an exponential increase of the prefactor with the energy barrier E in cases where the barrier E is large in comparison with kT as well as typical (phonon) excitation energies [10,11]. Since the Meyer-Neldel law is a many-body effect [10] the high value of the prefactor cannot be understood in terms of a single vibration frequency of the diffusing adatom.

To determine the parameters for diffusion over downward steps we follow the method introduced by Tersoff [12] and Bromann [5]. The method is based on the measurement of the nucleation rate Ω on top of previously grown adlayer islands as a function of island size and temperature. The adlayer islands were prepared by first depositing 0.06 ML at 280 K to produce a high island density and subsequent deposition of 0.15 to 0.25 ML at 500 K to grow the islands to the desired sizes. Because of the high island density determined in the first ("nucleation") step and the high temperature applied in the second ("growth") step, the growth rate of each island is small compared to the hopping rate of atoms along the island perimeter and flat islands with a shape close to the equilibrium shape (which is an almost perfect hexagon [13]) are produced independent of size. Finally, in a third ("test") step about 0.04 ML are deposited. Typical STM images before and after the final test step are depicted in Figs. 2(a) and 2(b). According to Ref. [12] the rate Ω, at which a new layer nucleates on top of the previously grown islands of radius R, is given as

$$\Omega = \frac{\sigma_1 \pi D}{3}\left(\frac{F}{4D}\right)^2\left[\left(R^2 + \frac{2RD}{h_S}\right)^3 - \left(\frac{2RD}{h_S}\right)^3\right], \tag{2}$$

where $D = h/4$ is the diffusion constant on the flat surface and $\sigma_1 \approx 3$ [2]. Rather than measuring Ω directly, the fraction

$$\begin{aligned} f &= 1 - \exp\left(-\int_0^t \Omega[R(t')]\,dt'\right) \\ &= 1 - \exp\left(-\int_0^\Theta \Omega[R(\Theta')]\,d\Theta'/F\right) \end{aligned} \tag{3}$$

of islands, on which a stable cluster has nucleated in the third step is evaluated. Figure 2(c) shows the fraction f as a function of island radius R for various temperatures in the final deposition step. A data fit yields $\Delta E = -53 \pm 23$ meV and $\nu_S = 3 \times 10^{12\pm0.3}$ s^{-1}. Because of the limited statistics the data scatter considerably,

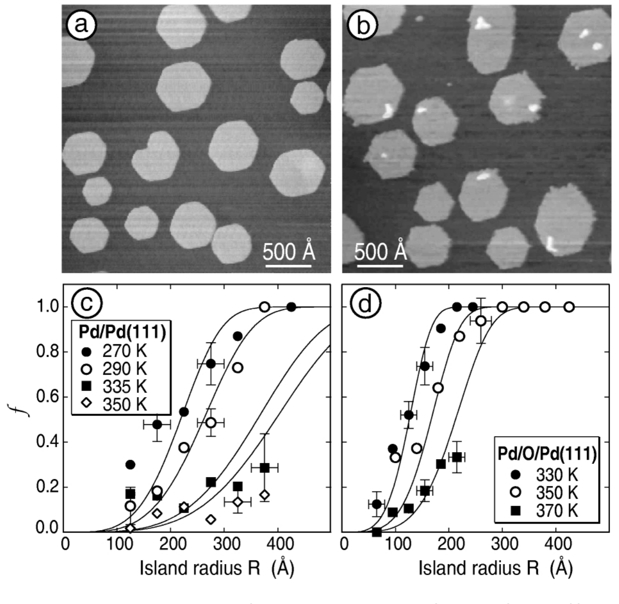

FIG. 2. Measurement of barrier and prefactor for diffusion over downward steps. STM images of (a) predeposited flat islands, (b) after additional deposition of 0.04 ML at 270 K. Fraction f of islands with a second layer on top as a function of the island size R for deposition on (c) clean and (d) oxygen-precovered Pd(111) at various temperatures. Symbols and lines denote experimental data and best fits, respectively.

in particular, at higher temperatures. However, the resulting uncertainty is included in the error limits of ΔE and ν_S as given above. Before discussing the values of ΔE and ν_S and their implications for the film morphology in more detail, it should be noted that the above analysis assumes the idealized case of circular islands with ΔE and ν being the same all around the island perimeter. However, in reality ΔE and also ν depend on the atomic arrangement at the island edge, i.e., the step orientations and the presence of kinks [14]. Hence the values given above represent suitably averaged, effective parameters. The negative value of the ES-barrier ΔE implies that diffusion over downward steps is energetically less hindered than diffusion on the flat terrace. While such behavior is hard to understand if diffusion occurs by ordinary hopping of the adatom over the step edge, an exchange mechanism provides a possible explanation: Here the diffusing adatom replaces in a concerted motion a step atom and pushes the latter in front of the step, thereby maximizing the bond energy in the transition state. *Ab initio* calculations for Pt(111) revealed that such a process is indeed the energetically most favorable one. A value of $\Delta E = +20$ meV was calculated [15], in rough agreement with the experimental value of 60 meV [16]. The values for platinum are quite small; however, the ES barrier for the related Pd system is lower, even negative. In Ref. [6] it was predicted that Pd(111) should have a particularly low ES barrier for interlayer diffusion, because the surface-state band is completely unoccupied. The present results substantiate this prediction.

The prefactor ν_S is 4 orders of magnitude lower than for diffusion on the flat surface. This further supports exchange as the relevant step-down diffusion mechanism. In case of such a concerted motion the transition state is highly ordered, resulting in a reduced entropy difference S_S between transition and initial state and hence in a reduced prefactor ν_S.

What are the implications of these parameters for the roughness of the growing film? To answer this question we follow Ref. [17] and recall that a rough film morphology results, if the fraction f of islands with a second layer on top takes a finite value before the islands coalesce. As the average island radius R depends on coverage Θ and F/h according to $\pi R^2 = \Theta/n_x$, with n_x given by Eq. (1), Eq. (3) can be rewritten as $f = 1 - \exp(-\Gamma)$ with [17]

$$\Gamma = \int_0^{\Theta} \tfrac{4}{3}\sigma_1 \pi a^6 \left[1 + 3\,\frac{B}{a} + 3\left(\frac{B}{a}\right)^2\right] d\Theta'. \qquad (4)$$

Here $a(\Theta') = [4^{1/3}\Theta'/4\pi\eta(\Theta')]^{1/2}$ and $B = F^{1/6}D^{5/6}/h_S$. Note that the deposition flux F and the hopping rates h_S and $h = 4D$ enter into Γ and hence the film roughness only through the ratio $B = F^{1/6}D^{5/6}/h_S$. Thus B provides a useful quantity to predict the changes in the film roughness brought about by altered deposition conditions (flux F; temperature T) or material parameters (energy barriers and prefactors). The higher B is, the rougher are the films. In particular, this implies that the temperature T enters into the surface roughness solely through $D^{5/6}/h_S \propto \exp[(\frac{1}{6}E + \Delta E)/kT]$. Hence, a temperature-independent film roughness is predicted in the special case where ΔE is negative with $\Delta E = -\frac{1}{6}E$. This condition is almost perfectly fulfilled for Pd/Pd(111) ($\Delta E = -53$ meV; $\frac{1}{6}E = 58$ meV). To characterize the film roughness we use the growth number w [18,19]. $w = 0$ indicates ideal layer-by-layer growth and $w = 1$ indicates ideal three-dimensional growth without interlayer diffusion. In Fig. 3 the experimentally determined film roughness w, as well as $B = F^{1/6}D^{5/6}/h_S$ are plotted for the growth of 5 ML Pd on Pd(111) [20]. We observe indeed a temperature-independent film roughness. As ΔE and ν are effective parameters derived for hexagonally shaped islands, whereas in the 5 ML experiments the islands change their shape with temperature from ramified λ-like to compact triangular [see Figs. 1(a) and 1(b)], the agreement between prediction and experiment is not a matter of course. It implies that although the overall shape of the islands is different, the microscopic nature of the steps is on average the same in all cases. It is especially noteworthy that the experiments yield quite rough film morphologies ($w \approx 0.6$) despite the negative ES barrier ΔE. This is a consequence of the low prefactor ν_S, which hinders an effective interlayer transport. In the spirit of transition-state theory the rough film morphology is thus of entropic rather than energetic origin in the present system. We note that the negative ES barrier ΔE is not a consequence of the unusually high value of the prefactor ν for diffusion on the flat surface. In contrast, a lower value of ν would imply an even more negative value of ΔE.

As a further cross-check the growth numbers w were also calculated from the experimentally determined diffusion parameters, by numerically solving the differential equations for the layer fillings as given by Meyer *et al.* [21]. In the temperature range between 200 and 400 K an almost constant value $w = 0.90 \pm 0.02$ is obtained, in

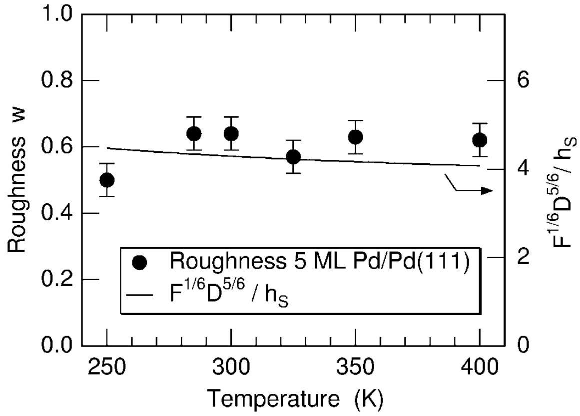

FIG. 3. Symbols: Experimentally determined film roughness as a function of temperature for growth of 5 ML Pd/Pd(111). Solid line: Plot of $F^{1/6}D^{5/6}/h_S$ (right-hand axis) versus temperature.

agreement with the expectation based on Eq. (4). The absolute value of the film roughness is higher in the calculations ($w \approx 0.90$) than in the experiments ($w \approx 0.60$). However, increasing the prefactor ν_S by a factor of 3 or lowering ν by a value of 4 (which is within the error margins of both prefactors) reproduces the experimentally observed film roughness.

The quantity B is especially useful in order to predict if a preadsorbed species can be used as a surfactant to flatten the film morphology [22]. For several systems oxygen was found to induce growth of flatter films [19,23,24]. Therefore we studied the effect of a preadsorbed oxygen $p(2 \times 2)$ overlayer in more detail. The diffusion parameters were determined in the same way as for growth on the clean surface. The data yield the following results: $i = 1$ up to at least 350 K [Fig. 1(d)], $E = 500 \pm 60$ meV, $\nu = 2 \times 10^{15\pm1.1}$ s^{-1} [Fig. 1(c)], $\Delta E = 70 \pm 35$ meV and $\nu_S = 1 \times 10^{14\pm0.5}$ s^{-1} [Fig. 2(d)]. Hence, oxygen increases both diffusion barriers, but also changes the prefactors by up to 2 orders of magnitude. Despite the increase of the ES barrier, flatter films are observed at room temperature ($w = 0.48$ instead of $w = 0.64$). However, this observation is in accordance with the change of B, which is lower for the oxygen precovered surface ($B = 3.0$ instead of 4.3). This lowering is brought about by the altered values of the prefactors: the increase of υ_S and the decrease of υ. Hence, in the present system the surfactant effect of oxygen is also of entropic origin [25].

A final comment concerns the possible role of surface contaminations. As shown recently, even minute amounts of adsorbates, in particular CO, can severely alter epitaxial growth [26]. However, in the present study the CO partial pressure always stayed well below 1×10^{-10} mbar. This is about a factor of 5 lower than in the earlier measurements for Pt/Pt(111) cited in Ref. [26]. Hence the influence of CO on the measured diffusion parameters should be significantly lower. More importantly, the validity of our conclusions about the importance of entropic effects for surface diffusion and epitaxial growth does not depend on the possible presence of contaminations.

In summary, the energy barrier for self-diffusion on Pd(111) is found to be exceptionally high (350 meV), while the ES barrier is even negative (−53 meV). Both observations are compatible with the recently proposed model about the influence of free-electron-like surface states on diffusion barriers [6]. The present work demonstrates that considering the energy barriers alone is not sufficient to understand the film morphology. Rather, entropic effects (i.e., different prefactors) must also be taken into account, thus deserving more theoretical attention [27,28].

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