Method for evaluation of the Ehrlich-Schwoebel barrier to interlayer transport in metal homoepitaxy

Ivan Markov*
Institute of Physical Chemistry, Bulgarian Academy of Sciences, 1113 Sofia, Bulgaria
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A method of evaluating the step-edge barrier which determines the rate of interlayer diffusion during homoepitaxial growth is developed on the basis of a full and general consideration of the problem of the critical island size for second layer nucleation. Data about saturation island density, critical surface coverage for second layer nucleation, the surface diffusion coefficient, and binding energies of the nuclei of the second layer are required to evaluate the barrier. The procedure includes evaluation of the size of the critical nuclei formed on top of the growing two-dimensional (2D) islands and the temperature interval in which the nucleus size does not change. The values 0.31 eV and 0.44 eV estimated for the step-edge barriers on Pt(111) at 425 and 628 K are attributed to (100) and (111) faceted steps, respectively. Assuming a change of the mechanism of descent from (111) faceted steps to a low-barrier one at about 450 K, we argue that the above values are in agreement with the experimentally observed inversion of shape of the 2D islands with the temperature [Michely et al., Phys. Rev. Lett. 70, 3943 (1993)].

I. INTRODUCTION

Epitaxial films are usually grown under far-from-equilibrium conditions. That is why kinetics play a prominent role in epitaxial growth. Two kinetic processes compete with each other during growth: surface diffusion and incorporation of adatoms into kink sites along steps.\(^1\) At higher temperatures surface diffusion is usually the slower process and determines the overall kinetics (diffusion regime of growth) whereas at low temperatures the incorporation of atoms into kinks controls the kinetics (kinetic regime of growth).\(^3\) Whereas an atom diffusing to an ascending step joins it upon striking (it has to overcome only the barrier for surface diffusion), an atom approaching a descending step has to overcome an additional barrier in order to join a kink at the step, owing to the reduced coordination.\(^2,3\) This additional step-edge barrier determines the velocity of interlayer transport and thus is of utmost importance to the mechanism of growth—multilayer or layer by layer (LBL)—and in turn to the morphology of the grown films. High barriers lead to enhanced nucleation on top of the growing islands and to rough interface of the grown films whereas low barriers for interlayer diffusion give rise to smooth interfaces.

Surface diffusion has been studied for a long time and is more or less well understood.\(^4,5\) It has been recently found that in addition to the traditional view of surface diffusion as a simple bridge-hopping event the adatoms on fcc(001) surfaces can perform diagonal (or “checkerboard”) hops in [100] direction.\(^6,7\) This is the so-called site-exchange (or concerted-substitutional) mechanism of surface diffusion.\(^4\) Total energy calculations of diffusion of Cu adatoms on Cu(001) (Refs. 8 and 9) showed that the barrier for site-exchange diffusion is approximately twice lower than that for bridge hopping. One could expect that the high-barrier bridge hopping mechanism takes place at high temperatures whereas at low temperatures the site-exchange diffusion with low barrier but also with lower prefactor prevails.\(^10\) Recent low-temperature experimental data on nucleation of Cu/Cu(001) (Refs. 11 and 12) could be explained on the basis of this assumption.\(^13\)

On the contrary, attachment of atoms into kink sites is still not comprehended although the measurements carried out by Ehrlich and Hudda\(^2\) 30 years ago showed that atoms joining a descending step should overcome an additional energetic barrier, \(E_s\). The theoretical study performed by Schwoebel\(^7\) of the impact of this discovery on the kinetics of crystal growth followed immediately. That is why this additional barrier is now known in the literature as a Schwoebel barrier. In this paper we call it the Ehrlich-Schwoebel (ES) barrier in order to give tribute to the experimental discovery of this phenomenon. Detailed field-ion microscopy (FIM) measurements of \(E_s\) in the case of Re, Ir, and W on W(110) gave values varying from 0.15 to 0.2 eV.\(^14\) The ES barrier on the surface of different materials has been a subject of numerous theoretical studies.\(^15-20\) In addition, several attempts have been made to evaluate the ES barrier from experimental data by using different approximations.\(^21-23\) In the present paper we suggest a general method for evaluation of the ES barrier from the critical island size for LBL growth, or in other words, the critical island size for second layer nucleation.\(^24,25\) No simplifications or additional approximations are made except for the assumptions of circular shape of the first layer islands and steady state diffusion profile on top of them. The approach includes naturally the evaluation of the size of the critical nucleus of the second layer and the temperature interval in which this size does not change. The only restriction of the method is that the island’s coalescence should be negligible so that the islands preserve more or less their circular shape. Thus the method is applicable to low critical coverages, or in other words, to low temperatures. The paper is organized as follows: The shape of the potential the adatoms sample at the step edge is considered in Sec. II. A general expression for the flux of atoms joining a descend-
ing step is derived in the same section. A full and general mathematical evaluation of the critical island size for second layer nucleation and the corresponding expressions for the ES barrier are given in Sec. III. The procedure of evaluation of the ES barrier including the evaluation of the size of the critical nucleus and the temperature interval in which it does not change is described in Sec. IV. An illustration of the method of evaluation of the ES barrier for descent at two temperatures on Pt(111) is given in Sec. V. The results are discussed and the method is compared with other methods in Sec. VI.

II. SHAPE OF POTENTIAL AT THE STEP EDGE

Wang and Ehrlich\textsuperscript{26} reported recently that incorporation of Ir atoms into a descending step on the Ir(111) surface can take place by the exchange (or push-out) mechanism [Fig. 1(b)] rather than by rolling over the edge [Fig. 1(a)]. Thus the last potential trough before the edge is shifted downwards below the level of the surface diffusion barrier and becomes asymmetric [Fig. 2(b)]. As a result the probability of joining the step becomes greater than the probability of going back to the terrace and the step becomes attractive rather than repulsive for atoms arriving from the upper terrace. In both cases $E_s$ is a measure of the asymmetry of the last potential trough. \textit{Ab initio} total energy calculations carried out by Stumpf and Scheffler\textsuperscript{15} of diffusion across steps on the Al(111) surface showed that the barrier for site exchange is much lower than that for rolling over the edge. Moreover, in this particular case the ES barrier for rolling over the edge is several times higher than the surface diffusion barrier $E_{SD}$ on the terrace.\textsuperscript{25} More detailed FIM measurements of Wang and Ehrlich\textsuperscript{27} have shown that the atoms are either repulsed from or attracted by the step from a distance of several atomic spacings. This means that approaching the step more than one potential trough become asymmetric. The nearest approximation in which only the last potential trough before the descending step is asymmetric is shown in Fig. 2. As shown in Fig. 2(b) the atoms can be trapped in the last potential trough and the probability of their joining the step is greater than their probability of returning back to the upper terrace. This is the potential profile found by Wang and Ehrlich in the case of Ir(111).\textsuperscript{28} On the contrary, the atoms in the last potential trough in Fig. 2(a) have a smaller probability of joining the step than going back to the terrace. The last potential trough in Fig. 2(a) could in general be shallower (curve 1) or deeper (curve 2) than that for surface diffusion on the terrace. If it is deeper the atoms trapped in it will tend to move along the edge at low temperatures and to go back to the terrace at higher temperature in accordance with the calculations of Villarba and Jönsson.\textsuperscript{19} Molecular dynamics studies of diffusion near the (100) faceted step showed that at 275 K the adatoms are trapped at the edge and sample only edge sites. At 425 K the adatoms prefer to diffuse backward onto the upper terrace rather than to descend to the lower terrace.\textsuperscript{19} The observation that when joining an ascending step on the Ir(111) surface the adatoms ‘‘feel’’ the step from a distance of two or three atomic spacings\textsuperscript{27} [schematically shown in Fig. 2(b)] has been theoretically calculated by Villarba and Jönsson in the case of Pt(111); they found that this effect is more pronounced at (100) faceted steps.\textsuperscript{19} During the process of growth the adatoms diffuse to the step edges and join kinks along them.\textsuperscript{28} A concentration of adatoms $n_a$ is formed in the near vicinity of the step, and it is higher than the equilibrium concentration $n_e$. The relative difference $\sigma_a = (n_a - n_e)/n_e$ is the driving force for the step propagation. The rate of propagation of the step is proportional to $\sigma_a$ and the proportionality coefficient is known as the kinetic coefficient of the step.\textsuperscript{1} Approaching a descending

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{fig1.png}
\caption{Schematic representation of the two mechanisms of descent: (a) rolling over the edge, and (b) site-exchange or push-out mechanism.}
\end{figure}

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{fig2.png}
\caption{Potential profiles the adatoms sample when joining descending steps. (a) Repulsive step at which the last potential trough is shifted upwards by an amount $E_s$, which is the Ehrlich-Schwoebel barrier. The last potential trough could be either shallower (curve 1) or deeper (curve 2) than the potential troughs far from the step. (b) Attractive step at which the last potential trough before the step is shifted downwards by an amount $E_s$ with respect to the level of the surface diffusion barrier. In both cases the upper terrace is on the left-hand side. The shallow potential trough on the right-hand side of (b) is in accordance with the FIM observations of Wang and Ehrlich and the theoretical calculations of Villarba and Jönsson (Ref. 19).}
\end{figure}
step the adatom will be trapped for a certain time in an asymmetric potential trough. At a temperature which is sufficiently high to allow diffusion across the step we can assume a steady state concentration of the atoms in the last potential troughs before joining the step. Then the incorporation of the atoms into the descending step will take place in two consecutive stages,

$$n_a = n_u = n_k,$$  \hspace{1cm} (1)

where $n_u$ and $n_k$ are the concentrations of atoms trapped in the last potential trough before joining the step, and the atoms detachable from the step (presumably, atoms in kink positions). Following the procedure given in Ref. 29 we find the net flux of atoms to the descending step to be given by

$$j = 2a n_u (n_u - n_e) \exp(-E_{SD}/kT)/(1+S),$$ \hspace{1cm} (2)

where $a$ is the spacing between the adsorption sites, $n$ is the vibrational frequency of the adatoms, and $S = \exp(\pm E_i/kT)$. The expression is valid for both repulsive and attractive steps. The plus sign ($S \gg 1$) refers to the traditional repulsive ES barrier [Fig. 2(a)], whereas the minus sign ($S \ll 1$) refers to the case shown in Fig. 2(b). At equilibrium $j = 0$ and $n_a = n_e$. If the last potential trough is symmetric, $S = 1$, the flux is exactly equal to the flux $j_0$ in the absence of Ehrlich-Schwoebel effect. In the case of attractive steps ($S \ll 1$) $j = 2j_0$, whereas at repulsive steps ($S \gg 1$) $j \ll j_0$.

### III. CALCULATION OF THE STEP-EDGE BARRIER

We consider a population of two-dimensional (2D) islands with circular shape and average radius $\rho$ and with a saturation density $N_s$. The surface coverage is small so that the islands do not contact each other and the coalescence is negligible. The islands grow at the expense of the atoms in between them and the atoms adsorbed on their upper surfaces. Two parallel processes—growth of the first monolayer islands and nucleation on top of them—compete with each other, which leads to the formation of nuclei of the second layer when the first monolayer islands reach a critical radius $\lambda$. The latter is thus proportional to the rate of growth of the 2D islands and inversely proportional to the frequency of nucleation on top of them. Expressions for $\lambda$ will naturally include in themselves the ES barrier which then can be estimated from them. Thus the critical radius $\lambda$ for second layer nucleation is defined as

$$\lambda = \frac{1}{2\pi} \frac{\partial}{\partial \rho} \int_0^\lambda \frac{\rho \Omega(\rho)}{v(\rho)} d\rho = 1,$$  \hspace{1cm} (3)

where $\Omega(\rho)$ is the nucleation frequency on the upper surface of the island and

$$v(\rho) = d\rho/dt = R/2\pi \rho N_0 N_s,$$  \hspace{1cm} (4)

is the rate of growth of the first monolayer islands in the case of complete condensation (absence or reevaporation) before nucleation on their upper surfaces occurs. The above equation follows from the condition of complete condensation $d\Theta/dt = 1$ where $\Theta = \pi \rho^2 N_s$ is the surface coverage, and $\tau = R t / N_0$ is the number of monolayers deposited, $N_0$ being the density of adsorption sites. The equation suggests that the size distribution of the islands is very narrow. This simplification facilitates the calculations without being crucial to the final results.

The frequency of nucleation on top of the islands is calculated through

$$\Omega(\rho) = 2\pi \int_0^\rho j(r, \rho) r dr,$$  \hspace{1cm} (5)

where

$$J(r, \rho) = \alpha_{i*} \nu N_0 \left( \frac{n_s(r, \rho)}{N_0} \right)^{i*+1} \exp \left( \frac{E_{i*} - E_{SD}}{kT} \right)$$  \hspace{1cm} (6)

is the nucleation rate on top of the islands which depends on the islands’ radius $\rho$ and the distance $r$ from the island center through the adatom concentration $n_s(\rho, \rho)$ on top of the islands. In the above equation $\alpha_{i*}$ is the number of ways an adatom can join the critical nucleus to produce a stable cluster, $G(i*) = 1$ is the Zeldovich factor, $E_{i*}$ is the work needed to dissociate the nucleus into single adatoms, and $i*$ is the number of atoms in the nucleus.

The adatom concentration $n_s(\rho, \rho)$ on top of the islands in the case of complete condensation can be found by solving the diffusion equation

$$\frac{d^2 n_s(r)}{dr^2} + \frac{1}{r} \frac{dn_s(r)}{dr} + \frac{R}{D_s} = 0$$  \hspace{1cm} (7)

subject to the boundary condition

$$j = -D_s \left( \frac{dn_s(r)}{dr} \right)_{r = \rho},$$  \hspace{1cm} (8)

where $R$ and $D_s$ are the atom arrival rate and the surface diffusion coefficient, respectively, and $j$ is given by Eq. (2). The integration of Eq. (7) gives

$$n_s(r, \rho) = n_e + \frac{R}{4D_s} \left\{ \rho^2 + \rho a (1 + S) - r^2 \right\}.$$  \hspace{1cm} (9)

Substituting $J(r, \rho)$ in Eq. (5) and carrying out the integration gives

$$\Omega(\rho) = \frac{\pi \alpha_{i*} R \exp(E_{i*}/kT)}{4(i*+2)N_0^{i*-1}} \left( \frac{R}{4D_s} \right)^{i*} \times \left\{ \left( \rho^2 + a \rho (1 + S) \right)^{i*+2} - \left( a \rho (1 + S) \right)^{i*+2} \right\}.$$  \hspace{1cm} (10)

The integration of Eq. (3) depends on the number of atoms in the critical nucleus. Therefore it is important to remember that on (111) surfaces of fcc metals $i*$ increases with temperature in the order 1, 2, 6, . . . , whereas on (100) surfaces the order is 1, 3, . . . 20. That is why we will solve the problem for $i* = 1, 2, 3, 6$.

Substituting Eqs. (4) and (10) into (3) and carrying out the integration gives for $i* = 1$ an equation of eighth power with respect to $\lambda$ which after rearrangement turns into a quadratic equation with respect to $(1 + S$). The solution, which is in fact the formula for the ES barrier, reads
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In the case of $i^* = 2$ we obtain a cubic equation with respect to $1 + S$ which can be easily solved. The result is

$$S = \frac{1}{a} \left( C_1 - \frac{0.2653}{a} \right)^{1/2} - \frac{6}{7} - 1, \quad (11)$$

with

$$C_1 = 192 \pi^2 D_s N_s^3/\alpha_s R N_0 \Theta_e^4,$$  

where $\Theta_e = \pi \lambda^2 N_s$ is the critical surface coverage for second layer nucleation.

In the case of $i^* = 2$ we obtain a cubic equation with respect to $1 + S$ which can be easily solved. The result is

$$S = \frac{\lambda}{a} \left( C_1^{1/3} - 0.4375 \right) - 1, \quad (13)$$

where

$$C_2 = 224 \pi^3 D_s N_s^3 \exp(-E_{\text{dim}}/kT)/\alpha_s R^2 \Theta_e^5,$$  

where $E_{\text{dim}} = E_{i=2}$ is the work to break a dimer bond.

In the case of $i^* = 3$ one obtains a quartic equation with respect to $1 + S$. An approximate solution valid for repulsive ES barriers only reads

$$S = \frac{\lambda}{a} \left( \frac{2}{15} C_3 \right)^{1/4} - 1, \quad (15)$$

where

$$C_3 = 7680 \pi^4 D_s^3 N_s^5 \exp(-E_3/kT)/\alpha_s R^3 \Theta_e^6,$$  

where $E_3 = E_{i=3}$. As mentioned above, Eq. (15) is valid for $C_3 > 1$. In the general case the resulting quartic equation

$$x^4 + ax^3 + bx^2 + cx + d = 0 \quad (x = 1 + S)$$

with coefficients $a = (16/9)(\lambda/a)$, $b = (5/8)(\lambda/a)^2$, $c = (8/11)(\lambda/a)^3$, and $d = (2/15)(\lambda/a)^4(1 - C_3)$, should be numerically solved.

Finally, in the case of $i^* = 6$ an equation of seventh power with respect to $S + 1$ is obtained whose approximate solution for $S \gg 1$ reads

$$S \approx \frac{\lambda}{a} \left( \frac{11}{144} C_6 \right)^{1/7} - 1, \quad (17)$$

where

$$C_6 = 73728 \pi^7 N_s^8 D_s^6 \exp(-E_6/kT)/\alpha_s R^6 \Theta_e^9.$$  

In the general case the resulting equation of seventh power

$$x^7 + ax^6 + bx^5 + cx^4 + dx^3 + ex^2 + fx + g = 0 \quad (x = S + 1)$$

with coefficients $a = (77/24)(\lambda/a)$, $b = (77/13)(\lambda/a)^2$, $c = (55/8)(\lambda/a)^3$, $d = (77/15)(\lambda/a)^4$, $e = (77/32)(\lambda/a)^5$, $f = (11/17)(\lambda/a)^6$, and $g = (11/144)(\lambda/a)^7(1 - C_6)$ should be numerically solved.

Using the above formulas the values of $S$ can be easily calculated from experimental data of $N_s$, $D_s$, $\Theta_e$, and $E_{i*}$. Note that the above parameters should be measured as precissily as possible as they enter the equations in very high powers and a small error in the measurements can cause a significant error in the final result. As will be shown below, the knowledge of the energies $E_{i*}$ of disintegration of the nuclei into single adatoms, as well as the energies to detach atoms from the stable clusters, are of crucial importance in estimating the ES barrier and the temperature intervals in which the nucleus size has a constant value.

IV. PROCEEDURE OF EVALUATION

In the case of Pt/Pt(111) Bott, Michely, and Comsa measured $\Theta_e$ and $N_s$ at two different temperatures—425 and 628 K. In order to evaluate the ES barrier we have to determine first the value of $i^*$ at the two temperatures. For this aim we use the following procedure. If there is no additional information about the nucleus size we assume first that $i^*$ has its lowest value $i^* = 1$ at the lower temperature $T = 425$ K and evaluate $S$ from Eq. (11). Then we calculate the critical temperature $T_1$, below which $i^* = 1$ and above which $i^* = 2$. In other words, we calculate the temperature above which the breaking of dimers becomes important.

The critical temperature of existence of a nucleus of size $i^*$ is calculated from the condition of stability of the cluster of size $i^* + 1$. The condition of stability of a cluster of any size $i$ is given by

$$\omega_i^- = \omega_i^+. \quad (19)$$

where

$$\omega_i^- = \beta_i \exp \left( -\frac{E_i - E_{i-1} + E_{SD}}{kT} \right) \quad (20)$$

is the probability to detach one atom from the cluster of size $i$, and

$$\omega_i^+ = \alpha_i D_s n_i(r = 0) \quad (21)$$

is the probability for one more atom to join the cluster, where $n_i$ is given by Eq. (9) with $r = 0$ and $\rho = \lambda$. The difference $E_i - E_{i-1}$ gives the work needed to detach an atom from a cluster of size $i$. Thus the work needed to break a dimer’s bond is $E_2 - E_1 = E_{\text{dim}}$, the work needed to detach an atom from a trimer on a (111) surface breaking two first neighbor bonds is $E_3 - E_2 = E_{\text{dim}}$, etc.

As mentioned above, $\alpha_i$ gives the number of ways of formation of a cluster of size $i + 1$ by joining an adatom to a cluster of size $i$, and $\beta_i$ is the number of ways of detachment of a single atom from a cluster of size $i$. A one-to-one correspondence exists between each decay process $i + 1 \rightarrow i$ and each growth process $i \rightarrow i + 1$, and hence

$$\alpha_i = \beta_{i+1}.$$  

Thus $\alpha_2 = \beta_3 = 6$ because every atom of the three-atom cluster has two possibilities to leave the cluster by bridge hopping in two directions. $\alpha_1 = \beta_2 = 4$ because each atom belonging to the dimer has two possibilities to leave the dimer by bridge hopping in two directions, and so on.

If $T_1$ is higher than the lower temperature our assumption that $i^* = 1$ is correct. If $T_1$ is lower than the higher temperature we evaluate $S$ from the higher-temperature data making use of Eq. (13). If our method is self-consistent one and the same value for $E_i$ should be obtained provided the islands are bounded by steps with one and the same structure and the mechanism of descent is one and the same at both temperatures. If this is not the case the values for $E_i$ calculated at low and high temperatures should be attributed to different step edges and/or to different mechanisms of descent. In order to check whether $i^* = 2$ at the higher temperature we calculate the second critical temperature $T_2$ above which...
FIG. 3. Dependence of the ES barrier on the average energy per bond in the critical nucleus. Curve 1 is according to Eqs. (13) and (14), \( T = 425 \) K and \( i^* = 2 \). Curve 2 is plotted by solving the equation of seventh power, \( T = 628 \) K and \( i^* = 6 \). The parameters included are taken from the paper of Bott, Michely, and Comsa (Ref. 35).

\( i^* = 6 \) and thus determine the temperature interval in which \( i^* = 2 \). \( T_2 \) is given by the condition of stability of a three-atom cluster (Eq. (19) with \( i^* = 3 \).

V. COMPARISON WITH EXPERIMENT

We illustrate the above method by calculating the ES barrier in the case of Pt(111). Bott, Michely, and Comsa \(^{35}\) found that at \( T = 425 \) K the second layer nucleation begins at a coverage \( \Theta_s = 0.3 \) with \( N_s = 3.37 \times 10^{10} \) cm\(^{-2}\) at \( R = 5 \times 10^{12} \) cm\(^{-2}\) s\(^{-1}\). At 628 K the above authors found that the second layer nucleation begins at \( \Theta_s = 0.8 \) with \( N_s = 3.5 \times 10^9 \) cm\(^{-2}\). Recent detailed measurements of Bott et al. \(^{36}\) showed that below 245 K dimer dissociation and mobility can be excluded. They also found a value of 0.26 eV for the surface diffusion barrier in excellent agreement with the FIM measured value \( E_{\text{SD}} = 0.25 \) eV (choosing \( \nu = 1 \times 10^{12} \) s\(^{-1}\)). \(^{37}\) Above 245 K, the dimers are either no longer stable or dimer diffusion takes place. Effective medium theory (EMT) calculations of Liu et al. \(^{38}\) gave anomalously small values, 0.13 and 0.16 eV, for the surface diffusion barriers of monomers and dimers on Pt(111), respectively. Although the dimer’s mobility cannot be a priori excluded it seems more reasonable to attribute the deviation of the data at 265 K found by Bott et al. \(^{36}\) to dimer bond breaking. If this is correct then most probably \( i^* = 2 \) at 425 K. As follows from Eq. (13) the knowledge of the bond breaking energy is of crucial importance for evaluation of the ES barrier. This is shown in Fig. 3 where the ES barrier is plotted vs \( E_{\text{bond}} \) for \( i^* = 2 \) (curve 1) and \( i^* = 6 \) (curve 2), with the help of the experimental data of Bott, Michely, and Comsa. \(^{35}\) In curve 1 \( E_{\text{bond}} \) represents the work needed to break a dimer whereas in curve 2 \( E_{\text{bond}} \) represents the energy per bond in a hexamer.

FIM studies and total energy calculations for series of metals showed that the crystal surface is “softer” than the bulk. \(^{3,10}\) Liu et al. \(^{38}\) have shown that when two Pt adatoms are bound together they are less able to form a tight bond to the substrate. The dimer bond length is shorter (2.56 Å) compared with the bulk value 2.77 Å and the dimer is located higher above the surface than a single adatom. Corrected effective medium theory calculations of Li and DePristo \(^{20}\) gave a value of about 0.75 eV for the work, \( E_{\text{dim}} \), needed to break a Pt dimer bond, a value of about 1.2 eV for the work, \( E_{\text{trm}} \), needed to detach an atom from a trimer on the Pt(111) surface, 1.6 eV for the work, \( E_{\text{bent}} \), needed to detach an atom from a closed shell heptamer, and \( E_s = 5.4 \) eV \((E_{\text{bond}} = 0.6 \) eV\) for the binding energy of a cluster consisting of six atoms. Assuming many body interactions in metals \(^{39}\) Nørskov et al. \(^{39}\) estimated twice lower values—\( E_s = 0.338 \) eV, \( E_{\text{trm}} = 0.647 \) eV, \( E_{\text{bent}} = 0.88 \) eV, and \( E_s = 2.7 \) eV \((E_{\text{bond}} = 0.3 \) eV\) respectively. If we accept the value for \( E_{\text{dim}} = 0.338 \) eV we find from curve 1 in Fig. 3 \( E_s = 0.37 \) eV, whereas the higher value of Li and DePristo gives \( E_s = 0.23 \) eV.

In order to avoid the above uncertainty connected with the choice of a value of \( E_{\text{bond}} \) we could estimate it from the island densities measured by Bott, Michely, and Comsa \(^{35}\) by using the well known expression for the maximum island density, \(^{40}\)

\[
N_s \approx N_0 \left( \frac{D}{F} \right)^{-\chi} \exp \left( \frac{E_{\text{bond}}}{(i^* + 2)kT} \right),
\]

where \( \chi = i^*(i^* + 2) \)

is the scaling exponent, \( D = v \exp(\gamma_{\text{SD}}/kT) \) is the hopping rate, and \( F = R/N_0 \) is the deposition rate per adsorption site. Using Eqs. (23) and (24) we obtain \( E_{\text{dim}} = E_s = 0.52 \) eV. In order to check this result we can estimate this parameter from the observation of Bott et al. \(^{36}\) mentioned above that at 265 K the dimers are already unstable. The lifetime of a dimer is given by \( 1/\omega_s \) where \( \omega_s \) is given by Eq. (20). The surface coverage of 0.1 monolayer (ML) is deposited with a rate \( R = 6.6 \times 10^{-4} \) ML/s and at 265 K the time interval during which dimers could break is 150 s. We thus find that in the temperature interval 245–265 K \( E_{\text{dim}} = 0.75 – 0.81 \) eV and \( E_{\text{dim}} = 0.49 – 0.55 \) eV, in good agreement with the above estimated value. The value 0.52 eV is nearly twice smaller than the energy to break a first neighbor bond as estimated from the heat of evaporation. For comparison the energy 0.25 eV for breaking a dimer bond on the Ag(111) surface is also twice smaller than the corresponding heat of vaporization. \(^{41}\) Although compatible with each other, both values for Pt and Ag dimers seem overestimated as compared with FIM measured values 0.32 eV (Ref. 42) and 0.285 eV (Ref. 43) of breaking of a W dimer on W(110). Then with \( E_{\text{dim}} = 0.52 \) eV we find \( E_s = 0.31 \) eV. Using Eqs. (19)–(21) gives for the critical temperatures \( T_1 \) and \( T_2 \) between which \( i^* = 2 \) the values 380 and 580 K, respectively. The lower limit is about 130 K higher than the experimentally established value. \(^{36}\)

Further, using Eqs. (23) and (24) with \( N_s = 5 \times 10^9 \) cm\(^{-2}\) at \( T = 628 \) K (Ref. 35) gives \( E_s = 4.5 \) eV or \( E_{\text{bond}} = 0.5 \) eV. The latter is in excellent agreement with the value 0.52 eV of the work to break a dimer bond.
Moreover, it is in accordance with the theoretical prediction of Li and DePristo\textsuperscript{20} and Nørskov et al.\textsuperscript{39} that the average energy per bond should decrease slightly with increasing cluster size. With $E_{\text{bond}}=0.5$ eV we estimate from curve 2 in Fig. 3 a value of 0.44 eV for the ES barrier at 628 K. It should be pointed out that the value $E_{\text{bond}}=0.3$ eV estimated by Nørskov et al. gives an anomalously high value of 0.7 eV for $E_s$, whereas the value 0.75 eV calculated by Li and DePristo is out of the interval of solutions of Eq. (17), i.e., it gives an unphysical value for $E_s$. Finally, from Eqs. (19)–(21) we find an upper limit $T_0=900$ K for the existence of nucleus size $i^* = 6$.

We finally check our assumption for a steady state diffusion profile on the island surface, or in other words, we neglect the movement of the island edge. The latter is determined by the condition $v_{\text{SD}}=aD$, where $v_{\text{SD}}=aD$ is the diffusion rate. Using Eq. (4) gives for $\rho = \lambda$

$$\frac{v_{\text{SD}}}{v(\rho)} = 2\Theta e^{-\lambda F}.$$  

$\Theta_e$ is of the order 0.2–0.8, $a/\lambda$ varies from 0.001 to 0.1, whereas the ratio $D/F$ is of order $1 \times 10^{-1} - 10^{-12}$. In the particular case considered above $D/F$ is of order $1 \times 10^{12} - 10^{13}$ at 425 and 628 K. Thus under typical conditions $2D/F$ always overcompensates $\Theta_e a/\lambda$ and $v_{\text{SD}}/v(\rho) \gg 1$. It thus follows that our assumption for a steady state diffusion profile is correct.

VI. DISCUSSION

Two different values—0.31 and 0.44 eV—have been obtained for the ES barrier at 425 and 628 K. These values are twice greater than the ones calculated by other methods.\textsuperscript{21–23} This is most probably due to the approximations and the additional assumptions made in the papers quoted. We will discuss this below. The step-edge barriers calculated in this paper for the case of (100) and (111) faceted steps on Pt(111) are both larger than the barrier of 0.25 eV (Ref. 37) for surface diffusion on the terrace. This is in agreement with a series of total energy calculations in the case of (111) surfaces of Pt (Refs. 18 and 19) and other fcc metals.\textsuperscript{15,20} The value obtained for $E_s$, at high temperature, and in turn at high coverage, for Pt(111) is probably slightly overestimated because of the considerable coalescence of the islands. A reasonable value should be of the order of 0.35–0.40 eV, but in any case we argue that it should be higher than the low-temperature value. We show below that the high-temperature value in the case of Pt(111) is in a qualitative agreement with experimental observations of Pt(111) growth.\textsuperscript{41}

Michely et al.\textsuperscript{44} reported that above 700 K the two-dimensional Pt islands have a hexagonal shape in which the islands are bounded simultaneously by (100) faceted (type A) steps and (111) faceted (type B) steps. This shape is preserved irrespective of the method of preparation (growth at 710 K or growth at 400 K and annealing at 710 K), and thus represents the equilibrium shape. If so, the exchange of atoms between steps and terraces is sufficiently fast, $n_a = n_e$, and the islands grow in a diffusion regime. The decrease of the temperature to 640 K leads to a disappearance of the A steps. The islands are bounded only by B steps and have a triangular shape. At temperatures as low as 400 K the islands have again a triangular shape but are now bounded by A steps. Thus we can attribute the higher value of 0.44 eV to the B steps and the lower value of 0.31 eV to the A steps. The inversion of shape takes place in a narrow temperature interval 450–470 K in which the islands have again a hexagonal shape and are again simultaneously bounded by A and B steps. The shape inversion can be explained only by the inversion of the rates of advance of both types of steps. The steps with higher rate of advance have to disappear from the growth shape of the islands.\textsuperscript{1} As mentioned above, the steps propagate by incorporating atoms approaching them on the upper and lower terraces. Assuming the flux of adatoms on the lower surface is one and the same for both A and B steps the difference of the rates of propagation is due solely to the flux on the island’s surface. As seen in Eq. (2), the latter is proportional to $\exp[-(E_{\text{SD}}+E_s)/kT]$. Therefore steps with higher barrier for interlayer transport will remain on the island’s shape. Accepting that $E_s^A < E_s^B$ explains readily the disappearance of A steps from the growth shape. The disappearance of the B steps at 400 K can be explained assuming that the reverse inequality $E_s^A > E_s^B$ is fulfilled. This inversion can take place by change of the mechanism of descent from a high barrier rolling over the edge to a low-barrier site exchange by analogy with the similar phenomenon on the crystal surface. We can assume that in the temperature interval 450–470 K part of the atoms roll over the B edge and the remaining part descend by site exchange. This results in an effective step-edge barrier which is approximately equal to the barrier at the A steps and the hexagonal shape reappears.

Following further the same logic we could speculate that even at lower temperature we could expect a change of the mechanism of descent to a low barrier one at the B steps too. Then the barriers at both kinds of steps become low (most probably lower than 0.2 eV) and the interlayer diffusion is again enhanced. The barrier for surface diffusion [0.25 eV (Ref. 37)] is now higher than the step-edge barriers and the islands again grow in a diffusion regime of growth.\textsuperscript{1,31} As a result low-temperature (or reentrant) layer-by-layer growth should reappear as has been observed by Kunkel et al. at about room temperature.\textsuperscript{45} If the low step-edge barriers were still higher than the surface diffusion barrier reentrant LBL growth should not be observed. This is probably the case of growth of Ag(111) where LBL growth has not been observed in the temperature range from 175 to 575 K.\textsuperscript{46} In this case scanning tunneling microscopy (STM) measurements showed that the surface diffusion barrier is very low, 97 meV,\textsuperscript{37} which is lower than the step-edge barrier of 120 meV as estimated at 150 K.\textsuperscript{23} The overall kinetics is controlled by the incorporation of atoms in kink sites and multilayer growth is observed in the whole temperature range. When one monolayer of Sb is deposited on top, the step-edge barrier is lowered, the growth takes place in a diffusion regime, and LBL growth is observed.\textsuperscript{48} Such an indium-induced lowering of the ES barrier has been experimentally established in the homoepitaxial growth of Cu(001).\textsuperscript{49} In general, the occurrence of the reentrant LBL growth requires the existence of two transition temperatures, which in turn requires three energy barriers. They could be either two surface diffusion barriers (high barrier with a high prefactor and low
barrier with a low prefactor) and one step-edge barrier, or two step-edge barriers (high and low) and one surface diffusion barrier, so that the surface diffusion coefficient at low temperature is larger than the interlayer diffusion coefficient. The low step-edge barrier at low temperature can be due to the small island size or the fractal shape of the islands as suggested by Kunkel et al.\textsuperscript{45}

As mentioned in the Introduction the evaluation of the ES barrier has been a problem of considerable interest in recent time.\textsuperscript{21–23} In all of these papers the same approach as in the present paper has been practically used and twice smaller values have been found. Meyer et al.\textsuperscript{21} assumed that the critical adatom concentration on top of the islands at the moment of the second layer nucleation is equal to the concentration between the islands. Equating the two concentrations they obtained the approximate expression (in the present notation)

\[
S = \frac{1}{2} \frac{\lambda}{a} \left( \frac{1}{\Theta_c} - 1 \right).
\]

As a result they found values of 0.15 and 0.165 eV for \(E_s\) in the homoepitaxy of Ag/Ag(111) and Pt/Pt(111) at 425 K, respectively. It should be pointed out that the assumption that the two concentrations mentioned above are equal is rather questionable. The adatom concentration on top of the islands depends on the island size, whereas the one in between the islands depends on the island separation. The asymmetry of incorporation of atoms into ascending and descending steps is another argument against the above mentioned assumption. The adatoms join ascending steps much more easily and the adatoms between the first monolayer islands should be consumed more than the atoms on the upper surface of the islands. If the above assumption was true then nucleation between the first layer islands should take place at the very high coverages at which second layer nucleation is established. Such nucleation could be registered as very small islands between the bigger ones or by much wider size distribution of the islands. The latter has not been observed. Šmilauer and Harris\textsuperscript{22} made the same assumption and obtained the same expression as above with the only exception that \(1/\Theta_c\) is replaced by \(4/\Theta_c\). As shown in the present paper, making additional assumptions is not necessary if the problem of finding of the critical island size Eq. (3) for second layer nucleation is solved.

Bromann et al.\textsuperscript{23} suggested a method for evaluation of the ES barrier based on measurements of the time evolution of the fraction of 2D islands on which second layer islands have nucleated. The procedure includes a fit of the experimental data with the equation for the fraction \(f\) of islands on which stable clusters have nucleated,\textsuperscript{25}

\[
f = 1 - \exp\left[-\int \Omega(\rho) dt\right],
\]

with two adjustable parameters—the ES barrier and the corresponding attempt frequency \(v\), \(\Omega(\rho)\) being given by Eq. (10). They found values of 0.12 eV with \(v = 1 \times 10^{13.5 \pm 1}\) s\(^{-1}\) and 0.03 eV with \(v = 1 \times 10^{9.5 \pm 1}\) s\(^{-1}\) for the systems Ag/Ag(islands)/Ag(111) and Ag/Ag(islands)/Pt(111), respectively. The ES barrier in the case of homoepitaxy of Ag is again higher than the surface energy barrier 0.097 eV. The very low barrier and particularly the low attempt frequency in the case of heteroepitaxy of Ag on Pt(111) suggest a site-exchange mechanism of descent.

In conclusion, we suggest a method for evaluation of the Ehrlich-Schwoebel barrier which determines the rate of interlayer transport, or in other words, the morphology of the growing film. The method is based on calculation of the critical island size for second layer nucleation. The procedure of evaluation includes calculation of the number of atoms in the critical nucleus, \(i^*\), of the second layer and the temperature interval in which the critical nucleus does not change its size. One or another expression for the ES barrier is obtained depending on the value of \(i^*\). An advantage of the method is that it does not require special experimental measurements and data fitting procedures. The only requirement is that no advanced coalescence is observed so that the islands preserve their circular shape. Values of 0.31 and 0.44 eV are found for the ES barriers at \(A\) and \(B\) steps in the case of Pt/Pt(111) at 425 and 628 K, at which \(i^*\) is equal to 2 and 6, respectively. The evaluation of the step-edge barriers requires knowledge of the binding and bond breaking energies. In the present paper the binding energies are estimated from experimental data on saturation island density. Once we have independently measured reliable data for these energies the ES barrier can be reevaluated. The larger value of the barrier at the \(B\) step on Pt(111) is probably overestimated owing to the advanced stage of coalescence of the islands at 628 K. However, it is in agreement with the disappearance of the \(A\) steps at 640 K. The inversion of the growth shape can then be explained by change of the mechanism of interlayer diffusion at the \(B\) steps. Assuming a change of the mechanism of descent at the \(A\) steps at as low as room temperatures leads again to a diffusion regime of growth and to reentrant LBL growth.

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\textsuperscript{a}Electronic mail address: imarkov@ipchp.ipc.acad.bg; Fax: (+359)-2-9712688.

\textsuperscript{1}A. A. Chernov, Modern Crystallography III (Springer, Berlin, 1984).


mentioning that Villarba and Jónsson considered as a kink atom an atom which belongs to the second row of atoms in the upper crystal plane. In fact the kink atom is the one at which the half row of atoms ends. Thus an atom in a kink (or half-crystal position) is bound to a half atomic row, half-crystal plane, and to the underlying half-crystal block (Refs. 1 and 31).