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Surface energetics from the transition from step-flow growth to two-dimensional nucleation in metal homoepitaxy

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Expressions for the critical temperature for transition from step-flow growth to growth by two-dimensional nucleation are derived for the cases of low and high barriers for step-down diffusion. The comparison of the equations with experimental data from diffraction studies of metal homoepitaxy makes possible the evaluation of either the energy to break first-neighbor bonds or the activation energy for step-down diffusion. The expressions are used to evaluate the bond energies and the Ehrlich-Schwoebel barrier for step-down diffusion in the systems Ag/Ag(001), Cu/Cu(001), Pd/Pd(001), Fe/Fe(001), Ag/Ag(111), Cu/Cu(111), and Pt/Pt(111). [S0163-1829(97)01143-0]

I. INTRODUCTION

Knowledge of energies on surfaces is of utmost importance for understanding the epitaxial crystal growth in atomistic terms. The mechanisms and the corresponding barriers and prefactors for terrace, step-down and edge diffusion, as well as the binding energies of clusters on surfaces determine the kinetics of growth and in turn the morphology of the growing epitaxial films and the quality of the devices based on them. Field ion microscopy (FIM) studies[1–4] and investigations of nucleation[5–7] have been for a long time the most used methods to extract information about the energetics on surfaces. This is the reason to look for other complementary methods which are sufficiently simple and reliable and do not require much experimental efforts.

It has been shown in numerous studies by using various diffraction techniques that vicinal surfaces of semiconductor [GaAs(001),[8–11] Si(001) (Refs. 12, 13)] and metal crystals [Ag(001),[14–16] Ag(111),[16,17] Cu(001),[18,19] Cu(111),[20–24] Fe(001),[25,26] Pd(001),[27,28] Pt(111) (Refs. 29, 30)] grow at sufficiently high temperatures by propagation of pre-existing steps (step-flow growth). As a result the intensity of the reflected beam remains constant. Below some characteristic temperature the diffusivity of the adatoms decreases and two-dimensional (2D) nucleation takes place on the terraces between the steps. The latter leads either to the appearance of oscillations,[8–16,18–21,25,27,29] or to a monotonic decrease of the intensity.[17,24] The critical temperature at which the intensity of the diffracted beam deviates from the constant value depends on the deposition rate and particularly on the miscut angle, or, in other words, on the terrace width.

The critical temperature for transition from step-flow growth to 2D nucleation is easy to measure and its theoretical interpretation can give information concerning the energy barrier for surface diffusion and the binding energies of the nuclei.[31–37] In neither of the above-mentioned papers has the existence of an additional energy barrier, which the atoms have to overcome when joining descending steps [the Ehrlich-Schwoebel (ES) barrier],[38,39] been accounted for. The problem of the critical temperature for step-flow growth accounting for the existence of the Ehrlich-Schwoebel barrier at the descending steps will be considered in this paper. The necessity of doing that arises from the marked difference in the behavior of the (100) and (111) surfaces of the fcc metals. In general oscillations of the diffracted beam intensity is observed on (100) surfaces,[14–16,18,19,27] although spot profile analysis of low-energy electron diffraction studies of the growth of the Cu(111) also showed high-temperature oscillations.[20,21] However, Wulfhekel *et al.* could not reproduce them by using thermal energy He scattering.[24] It has been also shown that the high-temperature oscillations in the homoepitaxy of Pt(111) observed by Kunkel *et al.*,[40] are due to a reconstruction of the Pt(111) surface.[42,43] The absence of oscillations on the fcc (111) surfaces can be attributed to the high ES barriers at the steps on this surface. On the other hand, the self-diffusion barriers differ considerably, being in general smaller on (111) surfaces. Thus a barrier of 0.03 eV for surface diffusion on Cu(111) has been measured,[24] which is an order of magnitude lower compared with 0.28 eV,[44] 0.40 eV,[45] 0.36 eV,[46] and 0.39 eV,[47] measured on Cu(001). It could be also added that both (001) and (111) surfaces differ considerably in adsorption energies and the energies to transfer an atom from the steps on the terraces. Thus the aim of the paper is to find reliable expressions for the critical temperature at which the step-flow growth is replaced by 2D nucleation, which could be used to extract data concerning energetics on surfaces.

II. CRITICAL TEMPERATURE FOR STEP-FLOW GROWTH

In all papers dealing theoretically with the transition from step-flow growth to 2D nucleation,[32–37] the authors calculate a critical number N_{cr} of nuclei between the steps which could give observable decay of the intensity of the reflected beams during the time of deposition of one monolayer. This approach has the following disadvantages. First, the critical density of nuclei which leads to an observable decay of the intensity is an unknown parameter which depends essentially on the instrumental resolution.[32] Iwanari *et al.* assumed that $N_{\mathrm{cr}}=1/\lambda^2$ where λ is the mean terrace width.[37] This assumption seems to be valid for small step separations of the order of 100–1000 Å (miscut angles 0.1–1°). It is difficult to ac-

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cept its validity when the terrace width is of the order of 10 000 Å as are the cases of Ag(111) (Ref. 16) and Fe/Fe(001).[25,26] In such cases $N_{\rm cr}$ should be larger than $1/\lambda^2$ and thus will be a more complicated function of λ. Second, a considerable Ostwald's ripening takes place at the high temperatures at which the transition is usually observed.[24] Small islands disappear at the expense of larger islands and the pre-existing steps. The latter favors the step-flow growth and thus masks the transition. What is more important is that the step-edge barrier changes only the distribution of the adatom population between the steps and does not influence perceptibly the average nucleation rate. As a result the ES barrier does not enter explicitly the expression for the critical temperature and cannot be evaluated.

When nuclei are formed between the pre-existing steps they begin to compete for adatoms. At higher temperatures the step density due to 2D islands is small and a large fraction of the adatoms still join the pre-existing steps. Obviously, a temperature exists at which the fraction of adatoms joining the 2D islands becomes equal to the fraction of adatoms joining the pre-existing steps. Below this temperature the surface grows mainly by formation and lateral spreading of 2D islands, the propagation of the pre-existing steps being strongly inhibited. Thus, a more correct approach should be the comparison of the fractions of the adatoms which join the pre-existing steps and the growing 2D islands of the first monolayer. Assuming these fractions are proportional to the density $1/\lambda$ of the pre-existing steps and to the density, $L(t)(\mathrm{cm}^{-1})$, of the steps belonging to a the first monolayer 2D islands, the above-mentioned approach reduces to a comparison of the step densities.

In the beginning of deposition the growth of the 2D islands leads to an increase of the density of the steps belonging to the first monolayer. At a later stage of growth a coalescence begins which leads to vanishing of the step density at the completion of the monolayer. Thus the step density displays a maximum $L_{\rm max}$ at a certain coverage $\Theta_{\rm max}$. Then the above-mentioned approach reduces to

$$L_{\rm max}=\frac{1}{\lambda}. \qquad (1)$$

In the case of a small ES barrier for step-down diffusion the atoms arriving on the surface of the 2D islands take part in the growth of the latter and the density of steps reaches its maximum value $L_{\rm max}$ at temperatures which are very near to the highest temperature at which oscillations of the intensity are observed. This is not, however, the case of a significant ES barrier. The adatoms striking the surface of the 2D islands cannot join their step edges, but nucleate and give rise to islands of the upper monolayers. As a result high pyramids (or cones) of growth are formed. The roughness of the growing surface increases sharply from the very beginning of the deposition and oscillations of the intensity are not observed. Instead, the latter decays monotonously with coverage (or time). In this case the first monolayer islands propagate more slowly in comparison with low ES barrier and a lower temperature is needed to produce such a density of steps surrounding the first monolayer islands which satisfies Eq. (1).

The maximum step density $L_{\rm max}$ can be easily calculated in both cases of negligible and significant ES barriers following in general the approach given by Stoyanov.[48] In both cases we consider the case of complete condensation. We assume that randomly spaced nuclei with a density N_s are formed in a short interval of time after the beginning of the deposition (instantaneous nucleation). The 2D nuclei grow further and give rise to compact rather than fractal 2D islands. The surface coverage Θ_1 of the first monolayer islands is then given by the solution of the well-known problem of Kolmogorov[49] and Avrami[50]

$$\Theta_1=1-\exp\left[-\pi N_s\left(\int_0^t v(t')dt'\right)^2\right], \qquad (2)$$

where $v(t)$ is the rate of lateral growth of the 2D islands.

In the time interval from t to $t+dt$ the surface coverage increases by $d\Theta_1$ and the radius of each island increases by $v(t)dt$. Then $d\Theta_1=L(t)v(t)dt$ or[48]

$$L(t)=\frac{1}{v(t)}\frac{d\Theta_1}{dt}, \qquad (3)$$

where $L(t)$ is the total periphery of all islands per unit area or the total step density of the growing 2D islands in time t.

Combining Eqs. (2) and (3) gives

$$L(t)=2\sqrt{\pi N_s}(1-\Theta_1)\sqrt{-\ln(1-\Theta_1)}. \qquad (4)$$

The total step density displays a maximum

$$L_{\rm max}=\sqrt{2\pi N_s/e} \qquad (5)$$

at a certain value of the surface coverage $\Theta_{\rm max}=1-\exp(-0.5)=0.393$, where e is the base of the Napierian logarithms. As seen $L_{\rm max}$ depends only on the density of islands. The latter can be determined by the condition of either the layer-by-layer (LBL) growth or the multilayer growth depending on the value of the ES barrier.

A. Low ES barrier

Layer-by-layer growth takes place when nuclei are formed on top of the 2D islands at the time of completion of the first monolayer. The condition is $\pi\Lambda^2N_s=1$, where Λ is the critical radius for second layer nucleation.[51,52] The critical radius Λ is defined by[51,53]

$$\int_0^\Lambda \frac{\Omega(\rho_1)}{v(\rho_1)}d\rho_1=1, \qquad (6)$$

where $\Omega(\rho_1)$ is the nucleation frequency on top of the first monolayer islands and $v(\rho_1)=R/2\pi\rho_1N_sN_0$ is the rate of growth of the 2D islands under the condition of complete condensation, N_0 and R ($\mathrm{cm}^{-2}\,\mathrm{s}^{-1}$) being the density of the adsorption sites and the rate of deposition, respectively. Making the substitution $t=\pi\rho_1^2N_sN_0/R$, the condition for LBL growth, $\pi\Lambda^2N_s=1$, reduces Eq. (6) to

$$\int_0^{t_1}\Omega(\rho_1)dt=1, \qquad (7)$$

where $t_1=N_0/R$ is the time of deposition of a complete monolayer. Equation (7) thus combines the definition of the critical island size for second layer nucleation with that for LBL growth and will be used below as a condition for ideal LBL growth.

The frequency of nucleation $\Omega(\rho_1)$ on top of the first monolayer islands is given by integration of the nucleation rate $J[n_s(r)]$ over the surface of an island with radius ρ_1,[51–54]

$$\Omega(\rho_1)=\int_0^{\rho_1} J[n_s(r)]2\pi r dr, \tag{8}$$

where the nucleation rate depends on the distance r measured from the island center through the adatom concentration $n_s(r)$. The latter is easy to find by solving the appropriate diffusion problem and reads[52,54]

$$n_s(r,\rho_1)=n_{se}+\frac{R}{4D_s}[\rho_1^2+a\rho_1 S-r^2], \tag{9}$$

where n_{se} is the equilibrium adatom concentration, a is the interatomic spacing, D_s is the surface diffusion coefficient, and $S=\exp(E_{\rm ES}/kT)$, $E_{\rm ES}$ being the additional Ehrlich-Schwoebel barrier the adatoms should overcome in order to join a descending step.

The nucleation rate is given by the expression[5,55–57]

$$J[n_s(r)]=\alpha_i D_s \frac{n_s^{i+1}}{N_0^{i-1}}\exp\left(\frac{E_i}{kT}\right), \tag{10}$$

where α_i is the number of ways an adatom can join the critical nucleus to produce a stable cluster consisting of $i+1$ atoms, and E_i is the work needed to dissociate the nucleus into single adatoms.

In the case of complete condensation the impinging atoms are distributed between the pre-existing steps and the 2D islands. Then at time t the surface coverage due to the 2D islands is given by

$$\pi\rho_1^2 N_s=\delta(t)\frac{Rt}{N_0}, \tag{11}$$

where $\delta(t)<1$ is the fraction of atoms which join the islands. The remaining fraction $1-\delta(t)$ join the steps. $\delta(t)$ is an increasing function of time beginning from 0 at ideal step-flow growth and approaches unity when the growth proceeds mainly by the growth of 2D islands. In the intermediate case which satisfies Eq. (1) we believe that $\delta(t)\approx 0.5$.

In the case of small ES barrier $(aS/\rho_1 \ll 1)$ we neglect the S-containing term in the brackets of right-hand side of Eq. (9). We substitute Eq. (9) into Eq. (10) and the latter into Eq. (8). We then express the radius ρ_1 through the time by using Eq. (11) and substitute the resulting expression for $\Omega(\rho_1)$ into Eq. (7). The integration and the rearrangement of the result gives

$$N_s=\frac{1}{2\pi}N_0 c_i^{-\chi/i}\left(\frac{D}{F}\right)^{-\chi}\exp\left(\frac{\chi E_i}{ikT}\right), \tag{12}$$

where $F=R/N_0$ is the deposition rate in units of monolayers (ML) per second, D is the hopping frequency of the adatoms,

$$\chi=\frac{i}{i+2} \tag{13}$$

is the familiar scaling exponent,[6,58–61] and

$$c_i=\frac{4(i+2)(i+3)}{\pi\alpha_i}. \tag{14}$$

Substituting Eq. (12) into Eq. (5) and the result into Eq. (1) gives after rearrangement

$$T_{\rm cr}=\frac{E_i+iE_{\rm sd}}{k\{\ln[c_i(\nu/F)^i]-2(i+2)\ln(\lambda/a\sqrt{e})\}}. \tag{15}$$

Equation (15) coincides with these derived by Fuenzalida with $i=1$,[36] and by Stoyanov,[32] and Iwanari *et al.*[37] under the assumption that $N_{\rm cr}=1/\lambda^2$. Having in mind that the assumption $N_{\rm cr}=1/\lambda^2$ appears as a lower limit for $N_{\rm cr}$ this coincidence is surprising. It is most probably due to the fact that the 2D islands compete for adatoms not only with the pre-existing steps but also between themselves. Only the islands which are in the close vicinity of the steps compete with the latter.

B. High ES barrier

The multilayer growth takes place when the second layer nucleation occurs before the completion of the first monolayer, i.e., $\pi\Lambda^2 N_s<1$. As a result several monolayers grow simultaneously. The larger the number of simultaneously growing monolayers the smaller is the amplitude of the oscillations of the intensity of the reflected beams. When the interlayer diffusion is negligible, $S\gg 1$, the frequency of nucleation on top of the growing islands is very high and towerlike structures are formed. The terraces between the islands on the nth and $n+1$st levels are very narrow and are comparable with the interatomic spacing. As a result the arriving atoms join the steps after several attempts. This is the extreme case of the kinetic roughness,[62] or *ideal multilayer or 3D growth* at which the oscillations of the intensity of the reflected beam vanish.

We accept that a definite number, n, of monolayers grow simultaneously and the condition for that is that the $n+1$st monolayer nucleates *when the first monolayer reaches completion*. Thus, the condition for multilayer growth has the same form as given by Eq. (7) with two exceptions. First, we should integrate to the time Nt_1, $(N>1)$, at which the first monolayer reaches, say, 99% of completion, and second, we should integrate the frequency of nucleation $\Omega(\rho_n)$ on top of islands belonging to the nth monolayer, whose coverage is, say, less than 1%. The condition for multilayer growth then reads

$$\int_0^{Nt_1}\Omega(\rho_n)dt=1. \tag{16}$$

In order to express the radius ρ_n as a function of time we have to calculate the surface coverage of the nth monolayer. For this aim we consider the formation of towerlike structures from the very beginning of the deposition. Assuming the interlayer diffusion is negligible all 2D islands grow at the expence of the atoms diffusing to them on the same terrace. The growth is described by a system of differential equations of the form given by Cohen *et al.*[63]

$$\frac{d\Theta_n}{d\tau}=\Theta_{n-1}-\Theta_n$$

$[\Theta_0(\tau)=1]$, which have to be solved subject to the boundary conditions $\Theta_n(\tau_n)=0$ where $\tau=Rt/N_0$ is the amount of the deposited material in a number of monolayers, and τ_n is the coverage at which the nth monolayer nucleates. Assuming $\tau_n \ll 1$ (the surface roughens very fast from the very beginning of deposition, $\pi\Lambda^2 N_s \ll 1$) the solution of the above system reads[63]

$$\Theta_1=1-e^{-\tau},$$

$$\Theta_2=1-(1+\tau)e^{-\tau},$$

$$\Theta_3=1-\left(1+\tau+\frac{1}{2}\tau^2\right)e^{-\tau},$$

$$\cdots,$$

or, in a general form

$$\Theta_n=1-e^{-\tau}\sum_{j=0}^{n-1}\frac{\tau^j}{j!}. \qquad (17)$$

As it has been shown by Cohen *et al.*[63] this mode of growth leads to an exponential decay of the intensity of the reflected beam ($I \propto e^{-4\tau}$) and to a rms roughness $\Delta=\sqrt{\tau}$. Thus, the above equations describe the ideal 3D growth. It is worth noting that the first monolayer reaches a completion at a coverage of approximately 5τ. At that coverage the step density $L_1(\tau)=e^{-\tau}\sqrt{\tau}$ vanishes.

The adatom concentration on top of the nth monolayer island is given again by Eq. (9) in which ρ_1 is replaced by ρ_n. In the case of high ES barrier, $aS/\rho_n \gg 1$, the difference $\rho_n^2-r^2$ can be neglected. This means that the adatom concentration varies negligibly with r and

$$n_s(r,\rho_n)\approx\frac{R}{4D_s}a\rho_n S. \qquad (18)$$

This is in agreement with the conclusion of Ehrlich,[64] that the adatom population on top of an island with repelling boundaries is uniformly distributed all over the island surface.

Substituting Eq. (18) into Eq. (10) and the latter into Eq. (8) gives after integration from 0 to ρ_n

$$\Omega(\rho_n)=\pi\alpha_i D_s N_0^2\left(\frac{RaS}{4D_sN_0}\right)^{i+1}\exp\left(\frac{E_i}{kT}\right)\rho_n^{i+3}. \qquad (19)$$

Having in mind that $\Theta_n=\pi\rho_n^2 N_s$, we expand Θ_n [Eq. (17)] in a Taylor series to the nth term and obtain $\Theta_n \approx \tau^n/n!$, or

$$\rho_n=\frac{\tau^{n/2}}{\sqrt{\pi N_s n!}}. \qquad (20)$$

Substituting Eq. (20) into Eq. (19) and the latter into Eq. (16) and carrying out the integration give after rearrangement

$$N_s=\frac{1}{4\pi}N_0\left(\frac{D}{F}\right)^{-\chi_S}\exp\left(\frac{\chi_S[E_i+(i+1)E_{\mathrm{ES}}]}{ikT}\right), \qquad (21)$$

where

$$\chi_S=\frac{2i}{i+3}. \qquad (22)$$

Numerical inspection of the effect of the values of N and n ($N=4$, $n=10$, or $N=5$, $n=12$) showed that the final result does not depend significantly on the values of N and n giving nearly a constant of 0.25. This circumstance has been used to simplify the final form of Eq. (21). The use of any other condition for multilayer growth, e.g., Eq. (7) with $N=1$ and $n=4$ changes only the pre-exponential factor making it slightly greater but not the scaling exponent and the energy term.

Finally, substituting Eq. (21) into Eq. (5) and the result into Eq. (1) gives after rearrangement

$$T_{\mathrm{cr}}=\frac{E_i+iE_{\mathrm{sd}}+(i+1)E_{\mathrm{ES}}}{k\{i\ \ln(\nu/F)-(i+3)\ln(\lambda/a\sqrt{2e})\}}. \qquad (23)$$

It should be emphasized that Eq. (23) is valid for the case of ideal 3D growth [Eq. (17)], which is characterized by an exponential decay of the intensity of the reflected beam proportional to $e^{-4\tau}$. This means that when comparing it with experimental data we have to take for T_{cr} the highest temperature at which $I/I_0=e^{-4\tau}$ or $\Delta=\sqrt{\tau}$ rather than the highest temperature at which the first decay of the intensity is observed.

III. COMPARISON WITH EXPERIMENT

As follows from Eqs. (15) and (23) in order to calculate the sums of the energies in the nominators we have to measure the critical temperature as a function of the mean terrace width. The critical size i appears as a free parameter which can be evaluated from additional measurements. We discuss briefly the first two parameters.

As discussed above the critical temperature in the case of systems showing intensity oscillations can be defined as the highest temperature at which the first oscillations are observed. The reasoning is that atoms impinging on the growing 2D islands join their steps and the latter compete for adatoms with the pre-existing steps from the very beginning of the deposition. The problem of finding T_{cr} in systems which do not show intensity oscillations is much more complicated. The atoms impinging on the growing islands do not join their steps but meet each other and give rise to nuclei of second, third, etc. monolayers. Thus they do not take part in the growth of the first monolayer islands and do not participate in the competition between the 2D islands and the pre-existing steps. As a result a partial step-flow growth occurs at temperatures lower than the highest temperature at which a decay of the intensity is observed. This means that the transition from step-flow to dominant 2D nucleation is a gradual one.[36] As mentioned above Eq. (23) has been derived under the assumption of ideal 3D growth which is characterized by exponential decay of the normalized intensity $I/I_0=\exp$

(-4τ) and a rms roughness $\Delta=\sqrt{\tau}$. This mode of growth is usually observed at lower temperatures.[24] Elliott *et al.* established the dependence $\Delta=\tau^{\beta}$ with $\beta=1/2$ at temperatures up to 300 K in the case of Ag/Ag(111) homoepitaxy. Beyond this temperature the exponent β decreases steeply and at 500 K it is smaller than 0.1.[16] Thus T_{cr} should be defined as the highest temperature at which $\Delta=\sqrt{\tau}$ or $I/I_0=\exp(-4\tau)$.

The terrace width depends first of all on the miscut angle. However, the pretreatment of the crystal prior to deposition plays a significant role. The pretreatment usually includes repeated cycles of ion (Ar^+, Ne^+) sputtering and annealing followed by a prolonged annealing at temperatures close to the melting point. All these lead to evaporation of material from the crystal surface. Thus 2 μm have been evaporated from the surface of Ag(111) during the pretreatment of the crystal prior to deposition.[16]

It is well established that the ES barrier leads to stability or instability of the equidistant train of steps in the sense of formation of bunches of steps coupled with much wider terraces than are expected from the miscut angle.[39,65] During growth the ES barrier stabilizes the step train making the steps equidistant. On the contrary, during evaporation the ES barrier leads to formation of bunches of more closely spaced steps separated by wider terraces.[65] This behavior could be expected from qualitative reasoning. If a growing step is lagging behind its normal (equidistant) position the length of the catchment area in front of it increases, and that behind it decreases. The front wider terrace contributes more to the total flux of atoms and overcompensates the loss of atoms from the upper terrace. As a result the step increases its velocity until both front and rear steps become equidistant. The opposite situation takes place during evaporation. It is now the upper terrace which is in front of the step. If the step lags the upper terrace becomes wider and the rear lower terrace becomes narrower. The step emits atoms more easily onto the lower narrow terrace and the total flux is reduced. The latter cannot be compensated by emitting on the upper terrace, the step decreases further its velocity and lags still more. This continues up to the moment when the rear terrace become so narrow that a significant repulsion of the neighboring steps compensate the effect of the ES barrier. As a result after a sufficiently long annealing a steady state will be reached such that the surface is resolved into bunches of steps similar to kinematic waves.[66] In other words, wide terraces and regions of much narrower terraces will alternate. What follows is that at higher temperatures nucleation will take place on the wide terraces but not on the narrow ones. Nucleation will occur on the narrow terraces at much lower temperatures. Thus a mixture of step-flow growth and 2D nucleation will occur up to some sufficiently low temperature.[67] This effect will be superimposed over the slow growth of the first monolayer islands and will make the transition even more gradual and in turn the critical temperature more difficult to define.

This is not, however, the case when the ES barrier is negligible. After the pretreatment the surface will preserve more or less the average step separation which is determined by the miscut angle. It should be emphasized that in some of the systems considered below the terrace width is measured (or estimated) with sufficient accuracy whereas in other systems it can be only guessed. In the latter systems the comparison with the experiment should be considered as an illustration of the method and the values obtained for the energy barriers should be taken with caution.

A. Systems with low ES barrier

In this subsection we consider systems showing oscillations of the intensity of the reflected beam and make use of Eq. (15).

1. Ag/Ag(001)

Suzuki *et al.* established a temperature of about 500 K beyond which reflection high-energy electron-diffraction (RHEED) intensity oscillations are not observed anymore.[14] The first clear oscillations have been detected at about 460 K. Unfortunately, the above authors did not report the terrace width on the substrate which has been prepared by deposition of 2000 Å Ag on MgO(001) single crystals. Bedrossian *et al.* confirmed this result on a crystal with a mean terrace width of 800 Å establishing clear oscillations at 400 K.[15] Assuming $i=3$ at $T\approx450$ K gives for the energy E_3+3E_{sd} the value 1.98 eV ($\nu=1\times10^{13}\ \mathrm{s}^{-1}$, $\alpha_i=8$, $F=0.0175$ ML/s). To the author's knowledge there are no experimental data concerning the cluster binding energy and the surface diffusion barrier for Ag(001) in the literature. Corrected effective-medium (CEM) calculations of Perkins and DePristo[68] give $E_{\mathrm{sd}}=0.46$ eV for the bridge hopping mechanism of diffusion, whereas the density-functional theory calculations of of Yu and Scheffler[69] gave slightly higher values of 0.52 eV. Using these values for E_{sd} results in values between 0.21 and 0.3 eV for the work to break a first-neighbor bond in a three-atom Ag cluster on Ag(001). They are comparable with the value of 0.25 eV obtained as a result of the nucleation study of Ag on W(110),[70] and 0.195 eV as calculated by effective-medium theory by Stoltze.[71]

2. Cu/Cu(001)

Critical temperatures of about 425 and 400 K have been found by de Miguel *et al.*[18] and by Ernst *et al.*,[19] both by thermal energy atom scattering, the separations of the preexisting steps being 425 and 700 Å, respectively. Using $E_{\mathrm{sd}}=0.4$ eV measured at 400 K,[45] we find the values 0.41 and 0.3 eV for the bond-breaking energy from the data of de Miguel *et al.* and Ernst *et al.*, respectively. These values are in accord with the embedded-atom method (EAM) calculated values of 0.37 eV (Ref. 72) and 0.43 eV (Ref. 73) for the dissociation energy of a Cu dimer on Cu(001) and with 0.46 eV found as a result of a nucleation study of Cu on Ni(001).[74]

3. Pd/Pd(001)

Flynn-Sanders *et al.* reported that at 500 K the intensity oscillations are lost entirely on a crystal surface with mean terrace width of approximately 200 Å.[27] With $i=3$ and $F=0.014$ ML/s one obtains $E_3+3E_{\mathrm{sd}}=2.53$ eV. The same authors measured also the activation energy for surface diffusion and found $E_{\mathrm{sd}}=0.61$ eV.[27,28] Thus, for $E_{\mathrm{bond}}\approx E_3/2$ one obtains the reasonable value of 0.35 eV.

4. Fe/Fe(001)

To the authors knowledge, this is the only bcc metal studied. Stroscio, Pierce, and Dragoset[25] observed very slowly damped RHEED intensity oscillations during growth of Fe/Fe(001) at 250 °C. Parallel scanning-tunneling microsscopy (STM) studies showed nearly perfect LBL growth. Assuming $i=1$ the interpretation of the STM investigations of the island density in the temperature interval 20–250 °C yielded an activation energy $E_{\mathrm{sd}}=0.45$ eV for surface diffusion and a prefactor 7.2×10^{-4} cm^2 s^{-1}. In a later study at temperatures higher than 250 °C (up to 356 °C) Stroscio and Pierce interpreted the island size distribution with $i=3$ and determined a binding energy $E_3=1.1\pm1.0$ eV of the critical nucleus, or 0.55 eV per bond.[26] Amar and Family interpreted the data of Stroscio and Pierce using an analytic expression for the island size distribution and estimated the value of 0.6 eV per bond in the critical nucleus.[75] Recently, Feibelman[76] criticized this value using the arguments that (i) the energy to break a W dimer on W(110) is about 0.3 eV as measured by FIM,[77,78] (ii) the cohesive energy of W is twice higher than that of Fe, and (iii) the neighboring atoms on Fe(001) are in fact second neighbors and the bonds between them should be much weaker. Assuming a change of the mechanism of diffusion with temperature from concerted substitutional diffusion[79] with a barrier 0.45 eV at low temperature to bridge hopping diffusion at high temperatures with a barrier of the order of 0.8 eV, Feibelman estimated a value of about 0.025 eV for E_{bond}.[76] Making use of Eq. (15) with $\lambda\approx10\,000$ Å,[25,26] and assuming $T_{\mathrm{cr}}=356$ °C we find $E_3+3E_{\mathrm{sd}}=1.47$ eV and $E_{\mathrm{bond}}=0.06$ eV (with $E_{\mathrm{sd}}=0.45$ eV) in accord with the arguments of Feibelman. We point out that we take as T_{cr} the highest temperature at which the authors observed 2D nuclei and that T_{cr} could be in fact higher than 356 °C. However, a temperature higher than 780 °C (1050 K) is needed to produce a value of 0.55 eV for E_{bond}, which is too high to be believed.

B. Systems with high ES barrier

Systems showing nonoscillatory behavior under the critical temperature for step-flow growth are considered in this section. Having in mind that the steps are usually nonequidistant owing to the crystal pretreatment we take in Eq. (23) as a rule the widest terraces. Besides, we define T_{cr} as the highest temperature at which exponential decay of the intensity ($I/I_0=e^{-4\tau}$) or rms roughness $\Delta=\sqrt{\tau}$ are established.

1. Ag/Ag(111)

Suzuki *et al.*,[14] Elliott *et al.*,[16] and van der Vegt *et al.*,[17] reported an absence of oscillations in a very wide temperature interval. In particular van der Vegt *et al.* have observed step-flow growth at temperatures above 575 K. The exponential decay $I/I_0=e^{-4\tau}$ of the intensity has been observed at a temperature as low as 225 K. On the other hand, Elliott *et al.* found that $\Delta=\sqrt{\tau}$ holds up to 300 K. As our model is valid for ideal 3D growth we will take this temperature as the critical one. At this temperature the islands have a compact rather than a fractal shape as shown by Wulfheckel *et al.*[24] With a terrace width of approximately 2400 Å as determined by the miscut angle of $<0.05°$ and $i=2$ ($\nu=1\times10^{13}$ s^{-1}, $F=0.02$ ML/s), for the sum of the energies in the nominator of Eq. (23) one obtains 1.0 eV. Accepting $E_2=E_{\mathrm{bond}}=0.25$ eV,[70] and $E_{\mathrm{sd}}=0.051$ eV,[80] gives $E_{\mathrm{ES}}\approx0.22$ eV, which is nearly twice larger than the 0.12 eV estimated by Bromann *et al.* who compared experimental data with the time dependence of the fraction of the islands on which second layer stable clusters have nucleated.[81] However, if we accept a terrace width of the order of 1 μm as reported by Elliott *et al.*,[16] Vrijmoeth *et al.*,[82] and Rosenfeld,[67] which is due to the pretreatment of the crystal prior to deposition as discussed at the beginning of this section, we obtain $E_{\mathrm{ES}}=0.15$ eV. The latter agrees better with that calculated by Bromann *et al.* Brune *et al.*[81,83] reported a nearly twice higher value for $E_{\mathrm{sd}}=0.097$ eV. If we take this value instead of 0.051 eV for the ES barrier one obtains 0.12 eV in excellent agreement with the value reported by Bromann *et al.* It should be pointed out that the dimer bond-breaking energy of 0.25 eV looks more reasonable as compared with the 0.45 eV of a Ag dimer on Ag(111) which has been found by CEM calculations.[84]

2. Cu/Cu(111)

As mentioned above Henzler[20,21] observed high-temperature oscillations in this case, whereas Dastoor *et al.*,[22] van der Vegt *et al.*,[23] and Wulfhekel *et al.*[24] established nonoscillatory decay of the intensity. Critical temperatures for occurrence of ideal 3D growth of 110 K,[22] 125 K,[23] and approximately 150 K,[24] have been established. To the best knowledge of the author, measurements of the rms roughness as a function of temperature as in the case of Ag/Ag(111) (Ref. 16) are not carried out. The analysis of the data of van der Vegt *et al.*[23] with $\lambda=120$ Å (miscut angle 1°), $F=0.00083$ ML/s, $E_{\mathrm{sd}}=0.03$ eV,[24] and $i=1$ gives $E_{\mathrm{ES}}=0.113$ eV. In this case the crystal has been annealed prior to deposition at low temperature 775 K compared with the melting point 1357 K, and formation of wide terraces is less probable. The data of Wulfhekel *et al.*[24] ($\lambda\approx1000$ Å, $F=0.006$ ML/s) give with $i=1$, $E_{\mathrm{ES}}=0.08$ eV. In this case, however, the crystal has been annealed at higher temperature (1000 K) and formation of wider terraces during the pretreatment cannot be excluded. Thus terraces 2000 Å wide have been observed by STM.[67] This gives even lower value for E_{ES} of the order of 0.055 eV. On the other hand, an Arrhenius plot of the mean island density as a function of temperature showed that the point at 140 K lies much lower than expected.[24] This could be interpreted as instability or surface mobility of the dimers as in the case of Pt/Pt(111).[85] E_{bond} can be evaluated from the data of Wulfhekel *et al.*[24] assuming instability of the dimers. The time allowed for breaking a Cu dimer on Cu(111) in the particular case ($\Theta=0.1$, $F=0.006$ ML/s)[24] is 17 s. Accepting $\nu=3\times10^{12}$ s^{-1} one obtains $E_{\mathrm{bond}}=0.38$ eV. Using EAM Breeman *et al.* estimated a slightly higher value 0.44 eV for the energy, E_{bond} to break a Cu dimer on Cu(111).[72] Assuming $i=2$, $\lambda=2000$ Å, and $E_{\mathrm{bond}}=0.38$ eV, we obtain $E_{\mathrm{ES}}=20$ meV which is too small to be believed. The latter means that most probably $i=1$ at 150 K. It should be stressed, however, that at the temperatures quoted above (110–150 K) the 2D islands have a fractal rather than a compact shape.[24] The latter could introduce an additional error.

3. Pt/Pt(111)

Poelsema *et al.* observed the appearance of oscillations at 800 K and $F=0.005$ ML/s.[29] The oscillations persisted up to temperatures as low as about 450 K. Below 340 K rapidly damping oscillations appeared again (reentrant layer-by-layer growth).[40,41] At medium temperatures between approximately 340 and 450 K ideal 3D growth has been established. It has been later found that the high-temperature oscillations can be attributed to reconstruction of the Pt(111) surface owing to the incorporation of the first deposited atoms into the uppermost atomic plane.[42,43] The reconstruction network inhibits the surface diffusion which in turn leads to formation of nearly an order of magnitude larger density of 2D islands. In absence of a reconstruction Pt grows 3D at high temperatures.[43] We could accept that the critical temperature for ideal 3D growth is 450 K. Then with $\nu=1\times10^{13}\ \mathrm{s}^{-1}$, $F=0.025$ ML/s,[85] and $i=2$,[54] one obtains $E_2+2E_{\mathrm{sd}}+3E_{\mathrm{ES}}=1.63$ eV. FIM measurements of the activation barrier for surface diffusion by Feibelman, Nelson, and Kellogg gave the value of 0.25 eV,[86] which is in excellent agreement with the value of 0.26 eV found by Bott *et al.*[85] from nucleation data. In addition the latter authors showed that above 245 K the saturated island density deviates from the straight line giving $i=1$. Assuming instability of the dimers above this temperature a value of approximately 0.5 eV for E_2 has been calculated.[54] The estimated value $E_{\mathrm{ES}}\approx0.21$ eV is lower than the 0.31 eV calculated by using the approach of the critical coverage for second layer nucleation.[54] The difference could be attributed to a possible inaccuracy in measuring T_{cr} owing to the surface reconstruction. An increase of the latter by 50 K gives a value of 0.27 eV.

IV. DISCUSSION

As shown above measurements of the critical temperature for step-flow growth allows the evaluation of energies on surfaces. A necessary condition is the knowledge of at least one of the energies entering Eqs. (15) and (23) from independent sources. Second, as precise as possible measurements of the terrace width (best with real-space techniques) appears as a necessary prerequisit for obtaining reliable results. In the case of a high ES barrier it is also necessary to measure the temperature for ideal 3D growth.

One very important question which has to be discussed in more detail is the island density given by Eq. (21). An equation very similar to Eq. (21) with the same scaling exponent (22) has been recently derived by Kandel.[87] In the latter case it was assumed that a significant barrier exists for attachment of an atom to the critical nucleus or 2D island. The result has been used to explain the observed high scaling exponents established in surfactant-mediated epitaxy.[88,89] However, comparatively large scaling exponents have been established also in cases where significant ES barriers are expected in the absence of surface active species. Thus Spiller *et al.* established scaling exponents 0.65 and 0.78 at 573 and 773 K, respectively, in nucleation of Ag/Ag(111)/W(110),[90] which were explained with very high values of i. Using the scaling exponent $\chi_S=2i/(i+3)$ gives $i=2$ at 773 K.

A scaling exponent of 0.85 has been established in the case of Si/Si(111)7×7 at 680 K in the absence of a surfactant.[88] Making use of a Stillinger-Weber potential Kodiyalam, Khor, and Das Sarma calculated significant ES barriers of 0.61 and 0.16 eV for diffusion over the [211] and [112] steps, respectively, on Si(111).[91] The above exponent has been interpreted with $i>6$,[88] whereas Eq. (22) gives $i=2$. The latter value seems more reasonable having in mind the comparatively low temperature (680 K) and that silicon is a very strong bonded material. The values of 1.7 eV (Ref. 92) and 2.3 eV (Ref. 93) have been reported for E_{bond}, the latter being taken as 1/2 of the heat of sublimation. A two-atom nucleus can be thought as consisting of an atom in the lower halflayer and an atom belonging to the upper halflayer both connected by a first-neighbor bond. The third atom which stabilizes the nucleus belongs again to the lower halflayer and is connected by first-neighbor bonds to the upper atom and to the underlying surface. This is a very stable configuration as an energy barrier of the order of 3.5–4.5 eV should be overcome in order to break simultaneously two first-neighbor bonds. Thus the mean time to break a single bond is of the order of seconds whereas millennia are required to detach an atom from the stable cluster consisting of three atoms at 680 K.

Using the rate-equation approach[6,58] Ratsch *et al.*[94] gave to the scaling exponent a more general form

$$\chi=\frac{i}{i(1+q-p)+2+q-p}, \tag{24}$$

which includes the dependence of the capture number σ_s of the growing islands on the proximity of adjacent islands and the way the island incorporate adatoms through $\sigma_s\propto N^q s^p$, where N is the island density and s is the number of atoms in the island. It is immediately seen that Eq. (24) turns into Eq. (22) accepting the combination $q=0$ and $p=0.5$. Bales and Chrzan discussed the problem within the framework of the mean-field rate-equation approach and concluded that for compact islands the capture number should have the form $\sigma_s\propto(Ns)^p$, i.e., $p=q$. Then the scaling exponent will be given by Eq. (13).[61] This is true for the diffusion regime of growth (slow diffusion and fast incorporation into steps) in the absence of a step-edge barrier when the islands ''feel'' each other through the overlapping diffusion fields.[95–97] It can be shown that the combination $q=0$ and $p=0.5$ is consistent with the assumption of a kinetic regime of growth (fast diffusion and slow incorporation of atoms into kink sites).[95–97] Indeed, when a significant step-edge barrier exists the adatoms are uniformly distributed between the islands (there is no overlapping diffusion fields),[65,95–97] the growing island does not ''feel'' the presence of the neighboring islands, i.e., $q=0$, and the rate of growth is proportional to the island's periphery, hence $p=0.5$.

The oscillatory behavior of systems at high temperatures does not mean that the ES barrier is absent at all. It could happen that at sufficiently low temperatures the nucleation occurs in a kinetic regime of film growth and $\chi=2i/(i+3)=1/2$ with $i=1$. At some higher temperatures i still can be equal to unity but the film growth takes place in a diffusion regime and $\chi=i/(i+2)=1/3$. All the above means that we can expect $\chi=1/2$ and $\chi=1/3$ in one and the same system depending on the temperature.

In summary, we have shown that the transition from step-flow growth to growth by 2D nucleation can be successfully used for evaluation of energetics on surfaces. The exact measurement of $T_{\rm cr}$ and λ is of crucial importance for obtaining reliable results. The critical temperature could be measured with more accuracy by varying the deposition rate at a constant temperature as done by Poelsema *et al.*[29] In the case of nonoscillatory behavior of the reflected intensity a measurement of the temperature dependence of the rms roughness should be carried out. The measurement of the interstep distance is more complicated owing to instrumental limitations. A possible inaccuracy could be avoided if after the high-temperature annealing a certain amount of the material is deposited at a temperature higher than $T_{\rm cr}$. Then the steps will become equidistant and the terrace width could be evaluated from the miscut angle with sufficient accuracy.

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