Adatom diffusion on vicinal surfaces with permeable steps

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Abstract: We study the behavior of single atoms on an infinite vicinal surface assuming certain degree of step permeability. Assuming complete lack of re-evaporation and ruling out nucleation the atoms will inevitably join kink sites at the steps but will do many attempts before that. Increasing the probability for step permeability or the kink spacing lead to increase of the number of steps crossed before incorporation of the atoms into kink sites. The asymmetry of the attachment-detachment kinetics (Ehrlich-Schwoebel effect) suppresses the step permeability and completely eliminates it in the extreme case of the infinite Ehrlich-Schwoebel barrier. A negligibly small drift of the adatoms in a direction perpendicular to the steps leads to a significant asymmetry of the distribution of the permeability events, the atoms thus visiting more distant steps in the direction of the drift. The curves are fitted with an exponential function containing a constant which can be considered as a length scale of the effect of the drift. Some conclusions concerning the stability of the vicinals are drawn.

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1. Introduction

Vicinal crystal surfaces grow by step flow when the temperature is sufficiently high such that the mean free path of the adatoms is longer than the mean terrace width. Lowering the temperature leads to a dramatic decrease of the adatom diffusivity, which gives rise to island nucleation and growth on the terraces [1, 2]. At sufficiently high temperatures the kink density along the steps is higher than the mean free path of the adatoms on the terraces and the steps represent continuous sinks for the adatoms [1]. With the decrease of the temperature the kink spacing increases and the step is no longer a continuous sink. The adatoms should follow a terrace-edge-kink mechanism to join the kinks. The latter involves consecutive processes of surface diffusion on the terraces towards the steps, diffusion along the step edges, and incorporation into kink sites [3, 4]. In this case atoms can leave the step before joining a kink site, or in other words, before joining the crystal lattice at least for the time of arrival of the next atom, which will bury the first one and which is a function of the supersaturation and diffusion rate. This phenomenon, known as a step permeability [5, 6], was observed in a series of material systems [7–9]. One could expect, for example, that

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the smooth $S_A$ steps on the vicinal surfaces of Si and Ge tilted at some small angle with respect to the singular (100) face will be much more permeable compared with the rough $S_B$ steps. The latter should contribute significantly to the transformation of the non-primitive vicinals consisting of alternating single layer $S_A$ and $S_B$ steps into the primitive surfaces consisting of only double layer, $D_B$, steps [10–12]. That is why the phenomenon of step permeability has been given considerable theoretical attention until now mostly in connection with the problem of bunching of steps on vicinal crystal surfaces [5, 13–16] and the critical terrace width for step flow growth [17, 18].

Growth at sufficiently high temperatures is accompanied by evaporation of atoms from the terraces. Thus an adsorption–desorption equilibrium takes place far from the steps [1] and the case is known as incomplete condensation [3]. At such temperatures the formation of two-dimensional nuclei on the terraces is less probable. However, at the growth temperatures usually used in experiments the re-evaporation of atoms is strongly inhibited. The reason is that the activation energies for desorption are usually of the order of the half of the heat of evaporation. We have then the case of complete condensation. At these lower temperatures the mean free path of the adatoms can become smaller than the terrace width and two-dimensional (2D) nucleation can take place. However, in most cases there is a temperature window in which the crystal surface grows by step flow and the 2D nucleation is still not possible (see Ref. [19] and the references therein).

Hence, the physics of both the cases of incomplete and complete condensation significantly differ particularly in connection with the problem of the step permeability. In the former case the atoms can leave the step and re-evaporate. In the latter case the atoms have no other choice but to stay on the surface. The rate of propagation of the separate steps is given by the simple relation $v = F\lambda$ where $F$ is the atom arrival rate per adsorption site and $\lambda$ is the mean terrace width [20]. Assuming some degree of permeability in the particular case of complete condensation means that if an atom does not join a kink site at a particular step it will do that at another step. If the permeability is zero the atom will join a kink at the first step which it meets. Increasing the degree of permeability from zero onwards (and ruling out the 2D nucleation) the number of steps the atom will cross without joining a kink will increase. Some steps can be visited only once, some steps several times but at the end of its journey the atom will inevitably join a kink site.

Filimonov and Hervieu performed a detailed microscopic analysis of the elementary processes taking place at a single step assuming the coefficients of step permeability and impermeability are complementary [6, 21, 22]. They found that a step is permeable if it is sufficiently smooth and the edge diffusivity is low. The natural result has been a coefficient $q = \delta_0/2\lambda$, which gives the ratio of the average equilibrium kink spacing $\delta_0$ and the mean free path of the atoms adsorbed at the edge, $\lambda = \sqrt{D_\text{e} \tau_\text{e}}$, where $D_\text{e}$ and $\tau_\text{e}$ are the edge atoms diffusion coefficient and the mean residence time of the atoms at the step edge, respectively. When $q \gg 1$ one can expect highly permeable steps and vice versa. Decrease of the temperature does not necessarily mean increase of the permeability due to smoothing of the step. The effect of the atoms’ edge diffusivity should be accounted for as well.

2. Results

In the present paper we are going a step further. We study the behavior of atoms on a vicinal surface consisting of infinite number of parallel steps and terraces assuming complete lack of re-evaporation and 2D nucleation. The steps are presumed to be smooth and the kinks are of one unit length $a$. The kink spacing (relative to interatomic spacing $a$) is distributed randomly by 20% around an equilibrium average value which is produced by a thermally activated process [1]. The attachment and detachment of atoms to and from step ledges is assumed initially symmetric as a first approach to the problem. The Ehrlich–Schwoebel effect [23, 24], or the attachment-detachment asymmetry, is then addressed. At the end we study the effect of a drift of the atoms on the terrace in a direction perpendicular to the steps either step-up or step-down [5, 25].

We perform a simple Monte Carlo simulation by making use of the following model. We consider a terrace with a square lattice and a single step (Fig. 1). Periodic bound-
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Figure 2. Distribution of the permeability events at each step before sticking to kink sites at different degrees of diffusivity \( f_e \) along the step ledge. The first descending step the atom meets to the right is numbered as the zeroth step. The steps to the left and to the right of it are given negative and positive numbers. We count the step crossings which accumulate at each step. \( \delta_0 = 150 \) Å.

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The collision of atoms at the step edge and the formation of kinks by kinetic one-dimensional nucleation \[26\] is ruled out. It should be pointed out that this assumption is valid at low deposition rates of the order of \(10^{13}\) cm\(^{-2}\) sec\(^{-1}\) which are usually used in MBE experiments under typical conditions \[17\]. With a typical tilt angle of about 0.1° the terrace width is approximately 800 Å and the rate of propagation of the step as calculated by the above formula is about \(8 \times 10^{-8}\) cm/sec. Bearing in mind that all atoms sooner or later join a step the flux of atoms to any step is \(j = v/a\), \[27\] which means that in each second 2 or 3 atoms join a step ledge with a length \(a\). The diffusion frequency is of the order of \(1 \times 10^8\) sec\(^{-1}\) (e.g. for Si(111) at 800 K \[28\]). In other words, the atom can make \(1 \times 10^8\) attempts to join a kink site or jump on the next terrace before the arrival of another atom. We conclude that the probability that two atoms collide under typical experimental conditions.

Three events are supposed to take place when an atom is adsorbed at the step ledge. It can either join a kink (impermeability event), or be reflected backward to the same terrace it came from, or cross the step going to the neighboring terrace (permeability event). The reflection of the atom on the same terrace that it has come from is not accounted for as a permeability event. We count as permeability events only the step crossings either from the upper to the lower terrace or from the lower to the upper one. Sticking of an atom to a kink site is assumed to be irreversible.

When an atom is adsorbed at the step ledge from the lower terrace four events are conceivable. The atom can either diffuse to the left and to the right along the ledge with equal probabilities \(f_e\), it can be reflected back to the lower terrace, or it can jump on the upper terrace (step crossing) with the probabilities \(f_{\text{forw}}\) and \(f_{\text{up}}\), respectively. The probability \(f_e\) is thus a measure of the atom diffusivity along the step ledge. When \(f_e = 0\), \(f_{\text{forw}} = f_{\text{up}} = 0.5\) and the step is highly permeable. In the opposite case \(f_e = 0.5\) \((2f_e = 1)\) the step is completely impermeable.

If an atom reaches the last adsorption site before the step from the upper terrace (the step rim) it can either jump down to be adsorbed at the step ledge with a probability \(f_{\text{down}}\), or can go back to the same terrace with the probability \(f_{\text{back}}\), or diffuse left and right along the step with the equal probabilities \(f_e\). All four probabilities are again complementary. Once the atom is adsorbed at the step ledge it has again the four probabilities mentioned above. Diffusing along the step rim the atom can also jump a kink site from above \[29, 30\].

Note that we work with probabilities rather than with activation energies relevant to the kinetic processes described above. Working with activation energies does not exclude the principle of complementarity of the corresponding frequencies so that the results would be the same. In addition, this approach makes the results valid for any materials of interest (metals, organics or semiconductors).

Fig. 2 shows the distributions of the permeability events at each particular step at a constant average kink spacing and at different values of the degree of ledge diffusivity \(f_e\). Symmetric attachment-detachment kinetics (absence of Ehrlich-Schwoebel effect, \(f_{\text{forw}} = f_{\text{up}}\) and \(f_{\text{back}} = f_{\text{down}}\)) is assumed. As seen the two neighboring steps which
border the zeroth terrace on which we deposit the atoms are crossed with equal probabilities. With increasing degree of permeability (decreasing $f_e$) more distant steps are crossed but the probability to cross the first two steps they meet also increases. This means that the atoms cross the first two bordering steps most of the times they visit more distant steps. The effect of the average kink spacing is shown in Fig. 3. The number of crossed steps increases with increasing step spacing at a constant degree of permeability. Again, by increasing the step permeability by increasing $\delta_0$ the atoms cross more distant steps but passing through the first two steps bordering the zeroth terrace.

Assuming asymmetry of the attachment-detachment processes at steps (Ehrlich-Schwoebel effect [23, 24]) decreases the step permeability dramatically (Fig. 4), but the curves remain symmetric. The number of the crossed steps, including the two steps which enclose the terrace, rapidly decreases. An infinite Ehrlich-Schwoebel barrier does not allow step crossings and the steps become completely impermeable irrespective of the mean kink spacing and the probability of step crossing or, equivalently, the step diffusivity. The result will be the same in the case of the inverse Ehrlich-Schwoebel effect.

It is instructive to follow the behavior of the average number of permeability events per atom, $\overline{N}$, as a function of the average kink spacing, $\delta_0$, at constant probabilities $f_e$ and $f'_e$ for diffusion along the step ledge and on the step rim, respectively. We sum up all the permeability events for each distribution curve shown in Fig. 3 and divide the sum by the number of atoms that have been released to perform diffusion on the vicinal surface. The result is shown in Fig. 5 in double logarithmic co-ordinates. As seen, perfect straight lines are obtained, which is an indication of a scaling of $\overline{N}$ with $\delta_0$. At probability $f_e$ going to zero (complete permeability) the slopes of the straight lines become very close to each other. The inset in Fig. 5 shows the slopes of the straight lines vs the probability $f_e$. The points are fitted by a simple exponential curve.

Fig. 6 demonstrates the effect of the directed drift of the adatoms on the distribution of the permeability events. A new step has been generated after each step crossing during the calculations. The curves naturally become asymmetric but most astonishing is the fact that a negligible bias of the order of 0.001 (the probability $f_{rw}$ in a direction step-down is 0.251 whereas in a direction step-up it is 0.249) causes a dramatic shift of the curves. The curves display long tails in the direction of the drift. Increasing the bias leads to decrease of the number of crossing of the
first step the atoms meet as the probability of going back is lower. The peak, however, always remains at the first step the atoms cross. The curves shown in Fig. 6 demonstrate an excellent fit with a simple exponential function of the kind $F(x) = \exp(-(x-1)/C)$ normalized to unity, where the parameter $C$ can be considered as a natural length scale of the tail. The constant $C$ is a linear function of the bias, where $C_{\text{bias}} = C_{\text{no bias}} - 0.25$, so that the exponential becomes

$$F(x) = \exp\left(-K\frac{x - 1}{C_{\text{bias}}}\right),$$

where $K$ is the reciprocal of the proportionality constant $C' = C/C_{\text{bias}}$. Unfortunately the length scale $C$ cannot be related to the wavelength of the bunching instability [31] owing to the oversimplified model used in the paper and the still unclear relation between the rate of the atoms drift and the dynamics of step bunching.

Fig. 2 shows that the total number of steps crossed in general small but the number of the permeability events is very large. The atoms prefer to go back and forth and to cross the same steps many times before joining a kink site. Even in the case of nearly complete permeability the atoms do not cross more than 15 steps on both sides of the zeroth terrace. The same conclusion can be made from Fig. 3. At the greatest mean kink distance of a thousand atomic spacings the atoms do not visit more than thirty steps. Thus, increasing the step permeability either by decreasing the step diffusivity or by increasing the mean kink spacing leads to a greater number of crossed steps. The latter is in agreement with the conclusions of Filimonov and Hervieu [6, 21, 22].

The influence of the Ehrlich-Schwoebel effect can be easily understood. The diffusion of the atoms is confined more and more in the single terrace on which they are deposited. The atoms are reflected from the ascending step and repulsed by the descending step. The atoms walk randomly on the same terrace and are repeatedly reflected by the same step until they join a kink site at the ascending step bordering the terrace. In the case of an inverse Ehrlich-Schwoebel barrier the atoms will join the descending step. An infinite Ehrlich-Schwoebel barrier will completely eliminate the step permeability.

The curves $\tilde{N}$ vs $\delta_0$ can be described by the relation $\tilde{N} = A\delta_0^{\alpha}$, where the slope of the log-log plot, $\alpha$, is an exponential function of the diffusivity of the atoms, $f_\text{a}$, along the step ledge (see the inset in Fig. 5). At small values of $f_\text{a}$ the slopes $\alpha$ saturate as the steps become so permeable that the atoms do not feel the difference in mean kink spacing. The case is opposite when the step diffusivity becomes very large. The steps become highly impermeable which can be compensated by larger and larger mean kink spacing.

The bunching of steps on crystal surfaces was observed for the first time in the case of Si [32]. The phenomenon was explained by a drift of the atoms in one direction owing to a force which originates from the direct current applied to heat the crystal [25]. Comparison of the experimental data with the theory showed that the force exerted on the adatoms is very small [33]. This conclusion is compatible with the negligibly small values of the bias leading to the curves shown in Fig. 6.

In general, the diffusion of atoms on a vicinal surface with permeable steps is influenced mostly by the attachment-detachment kinetics (either symmetric or asymmetric) and the widths of the neighboring terraces. The existence of an Ehrlich-Schwoebel effect reduces strongly the step permeability confining the atom diffusion to a single terrace. In the case of equidistant steps and symmetric attachment-detachment kinetics the adatom concentrations on both sides of the steps are equal. There is no gradient of the concentration and the rates of step crossings of ascending and descending steps are equal [18, 34]. This results in a dynamic equilibrium of step crossings in both directions which is not expected to have an effect on the surface stability as it leads to an effective vanishing of the step permeability. If however the steps are not equidistant and neighboring terraces have different widths the adatom concentrations on both sides of a step will have different values (greater on the side of the wider terrace). Then a net flux of atoms from the wider to the narrower terrace will take place. The latter could either lead to stabilization of the vicinal surface or to pairing of steps depending on the permeability of the separate steps.
3. Conclusions

In summary, we studied the behavior of adatoms on a vicinal surface with permeable steps. We assumed a complete lack of re-evaporation and ruled out the two-dimensional nucleation. We have found that the atoms visit comparatively small number of steps going back and forth on the vicinal and cross multiply one and the same steps before joining a kink site. The Ehrlich-Schwoebel effect strongly diminishes the step permeability confining the migration of the adatoms to a single terrace. Very large Ehrlich-Schwoebel barriers should completely eliminate the step permeability. The mean number of permeability events per atom shows a scaling law with the mean distance between the kinks. A negligible drift of the atoms in a direction perpendicular to the steps makes the distribution curves strongly asymmetric. The curves display long tails in the direction of the drift which have exponential-like behavior. In any case, the step permeability should not change the rate of step propagation $v = F\lambda$ as the atoms inevitably join kink sites although not in the first step they meet.

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References

[1] W. K. Burton, N. Cabrera, F. C. Frank, Philos. Tr. R. Soc. S-A 243, 299 (1951)
[2] J. Krug, In: A. Voigt (Ed.), Multiscale Modeling in Epitaxial Growth (Birkhäuser, 2005), 70
[3] J. A. Venables, Introduction to Surface and Thin Film Processes (Cambridge University Press, 2000)
[4] A. Chernov, Modern Crystallography III, Crystal Growth (Springer Verlag, Berlin, 1984)
[5] S. Stoyanov, V. Tonchev, Phys. Rev. B 58, 1590 (1998)
[6] S. N. Filimonov, Yu. Yu. Hervieu, Surf. Sci. 553, 133 (2004)
[7] B. Voigtländer, T. Weber, Phys. Rev. Lett. 77, 3861 (1996)
[8] S. Tanaka, N. C. Bartelt, C. C. Umbach, R. M. Tromp, J. M. Blakely, Phys. Rev. Lett. 78, 3342 (1997)
[9] F. Buatier de Mongeot et al., Phys. Rev. Lett. 91, 016102 (2003)
[10] D. J. Chadi, Phys. Rev. Lett. 59, 1691 (1987)
[11] B. S. Swartzentuber, Y. W. Mo, R. Kariotis, M. G. Lagally, M. B. Webb, Phys. Rev. Lett. 65, 1913 (1990)
[12] O. L. Alerhand, D. Vanderbilt, R. D. Meade, J. D. Joannopoulos, Phys. Rev. Lett. 61, 1973 (1988)
[13] M. Sato, M. Uwaha, Y. Sato, Phys. Rev. B 62, 8452 (2000)
[14] M. Sato, Eur. J. Phys. B 59, 311 (2007)
[15] O. Pierre-Louis, Phys. Rev. E 68, 021604 (2003)
[16] O. Pierre-Louis, C. R. Phys. 6, 11 (2005)
[17] W. F. Chung, K. Bromann, M. S. Altman, Int. J. Mod. Phys. B 16, 4353 (2002)
[18] B. Rangelov, M. S. Altman, I. Markov, Phys. Rev. B 75, 245419 (2007)
[19] I. Markov, Phys. Rev. B 56, 12544 (1997)
[20] J. Villain, J. Cryst. Growth 275, e2307 (2005)
[21] S. N. Filimonov, Yu. Yu. Hervieu, Phys. Low-Dimens. Str. 7/8, 15 (2002)
[22] S. N. Filimonov, Yu. Yu. Hervieu, Surf. Sci. 507-510, 270 (2002)
[23] G. Ehrlich, F. G. Hudda, J. Chem. Phys. 44, 1039 (1966)
[24] R. L. Schwoebel, E. J. Shipsey, J. Appl. Phys. 37, 3682 (1966)
[25] S. Stoyanov, Jpn. J. Appl. Phys. 30, 1 (1991)
[26] V. V. Voronkov, Sov. Phys. Crystallogr. 15, 13 (1970)
[27] I. Markov, Crystal Growth for Beginners, Fundamentals of Nucleation, Crystal growth and Epitaxy, 2nd edition (World Scientific, 2003)
[28] B. Voigtländer, A. Zinner, Surf. Sci. 292, L775 (1993)
[29] J. Tersoff, A. W. Denier van der Gon, R. M. Tromp, Phys. Rev. Lett. 72, 266 (1994)
[30] M. Villarba, H. Jónsson, Surf. Sci. 317, 15 (1994)
[31] F. Leroy, P. Müller, J. J. Metois, O. Pierre-Louis, Phys. Rev. B 76, 045402 (2007)
[32] A. Latyshev, A. Aseev, A. Krasilnikov, S. Stenin, Surf. Sci. 213, 157 (1989)
[33] K. Fujita, M. Ichikawa, S. Stoyanov, Phys. Rev. B 60, 16006 (1999)
[34] M. Ozdemir, A. Zangwill, Phys. Rev. B 45, 3718 (1992)