Breakdown of step-flow growth in unstable homoepitaxy

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PACS. 81.10.Aj – Theory and models of crystal growth.
PACS. 68.55.Ac – Nucleation and growth: microscopic aspects.
PACS. 05.70.Ln – Nonequilibrium and irreversible thermodynamics.

Abstract. – Two mechanisms for the breakdown of step flow growth, in the sense of the appearance of steps of opposite sign to the original vicinality, are studied by kinetic Monte Carlo simulations and scaling arguments. The first mechanism is the nucleation of islands on the terraces, which leads to mound formation if interlayer transport is sufficiently inhibited. The second mechanism is the formation of vacancy islands due to the self-crossing of strongly meandering steps. The competing roles of the growth of the meander amplitude and the synchronization of the meander phase are emphasized. The distance between vacancy islands along the step direction appears to be proportional to the square of the meander wavelength.

Introduction. – Growing surfaces are commonly divided into two classes, vicinal or singular [1–3]. On vicinal surfaces the density of atomic steps, originating from the miscut of the sample, is high, so that most of the atoms arriving on the surface attach to these steps and the nucleation of adatom islands on the terraces may be neglected. The crystal then grows in the step-flow mode, simply by propagation of the steps. As no new steps appear, all the steps have the same sign, and the surface profile remains monotonic in the direction of vicinality. Even if the step morphology is unstable against step meandering, the growth may be considered as a two-dimensional problem.

It has been observed however in experiments [4,5] as well as in computer simulations [4,6,7] that the step-flow mode is only metastable. Eventually steps having a sign opposite to the original vicinality appear on the surface. This destroys the two dimensional character of the growth and leads to the formation of genuinely three-dimensional structures.

Steps of opposite sign may originate from two different mechanisms: either from the nucleation of adatom islands on the terraces, or through the formation of vacancy islands. Island nucleation on the terraces is severely suppressed by the steps as they collect the deposited adatoms, keeping the adatom concentration low. Due to fluctuations, however, some nucleation events do occur. Nucleation of islands on the terraces alone is not enough to destabilize

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the step-flow growth, as the islands collide with the propagating steps and merge with them. The step-flow growth is destabilized only if new islands are nucleated, on the average, on top of the terrace islands before the latter are incorporated into the steps.

Vacancy islands can be formed on the terraces due to the meandering of the steps. During growth the atomic steps often do not remain straight, but form a meander pattern [5,8] either due to the Bales-Zangwill (BZ) instability [9], or due to a Kink-Ehrlich-Schwoebel effect (KESE) [10,11]. As the meander amplitude becomes large in the course of time, it is plausible that a step might cross itself forming thus a closed loop, i.e. a vacancy island. Before turning to the detailed analysis of this effect, which forms the main subject of this Letter, we briefly discuss destabilization due to the nucleation of islands.

Mound formation through terrace nucleation. – A common criterion for step-flow growth is that the step distance $\ell$ should be smaller than the nucleation length $\ell_D$, the distance between the nucleation centers on a singular surface; for irreversible aggregation $\ell_D \sim (D/F)^{1/6}$, where $D$ is the adatom diffusion coefficient and $F$ is the deposition flux [1,2]. When $\ell \ll \ell_D$ essentially all atoms go to the existing steps and nucleation events are very rare. Due to fluctuations in the deposition beam, however, nucleation of adatom islands occurs also during step-flow growth. When $\ell$ is not too much smaller than $\ell_D$, islands are continuously nucleated on the terraces and incorporated into the steps. The nucleation length is altered by the presence of the steps and becomes $\ell_D \approx (D/F)\ell^{-5}$ parallel to the steps [12,13]. Coalescence of the terrace islands with the steps also affects the step morphology [13].

Nucleation of islands on the terraces is not enough to launch mound formation. It is also required that, on average, a new island will be nucleated on top of the terrace island before it is incorporated into the step, because this process must be repeated several times when a mound starts to form. Nucleation on top of islands is enhanced by an Ehrlich-Schwoebel (ES) barrier, which prevents the descent of adatoms across steps [14]. The strength of this effect depends on the ratio of the ES-length $\ell_{ES} = D/D'$, where $D'$ is the interlayer hopping rate, to the island radius $R$ [2,3]. When $\ell_{ES} \ll R$ second layer nucleation on a singular surface does not occur until the first layer islands have started to coalesce, at $R \approx \ell_D$, and the initial growth proceeds layer by layer; on a vicinal surface this implies that second layer nucleation is preempted by incorporation of the first layer islands.

Destabilization of step flow growth by mound formation thus requires a strong ES effect, in the sense that $R \ll \ell_{ES}$ at the time of incorporation. To obtain a quantitative criterion, we start from the expression $\omega(R) = \pi^2 F^2 R^3/2D'$ for the nucleation rate on top of an island of radius $R$, which holds for strong ES barriers and irreversible nucleation [15]. The probability that nucleation has occurred on the island within a time $t$ after its creation is then

$$p_{\text{nuc}}(t) = 1 - \exp \left[ -\int_0^t \omega(R(s))\,ds \right],$$

where $R(t)$ is the island radius at time $t$. Mound formation requires that $p_{\text{nuc}}$ grows to order unity, say $p_{\text{nuc}} = 1/2$, during the time $t^*$ that the step needs to travel a distance $\ell/2$, and hence to engulf the island. As the step velocity is $v_{\text{step}} = F \ell$, we have $t^* = 1/(2F)$. We further assume that half of the material landing on a terrace segment of length $R$ contributes to the growth of the island, so that $R(t) = F\ell t/2$. Evaluating (1) and setting $p_{\text{nuc}}(t^*) = 1/2$, we find that mound formation occurs when

$$\ell > \ell_c \approx 4.4 \times (D'/F)^{1/5}.$$  

The length scale $\ell_c$ has the same dependence on the growth parameters as the radius of the top terrace of a mound growing on a singular surface [2,15], though the dimensionless prefactor is
somewhat larger. Note that since for strong ES barriers $\ell_c \ll \ell_D$, the condition does not contradict the conventional step flow criterion $\ell \ll \ell_D$.

This analysis assumes that steps are straight and equidistant, and that the nucleation events on the terraces are uncorrelated. In reality the step train may suffer from growth instabilities either in the step direction (step meandering) [3,8–11,16] or in the direction of the vicinality (step bunching) [1]: sometimes the two instabilities even coexist [17]. In the case of step bunching the large terraces forming between the bunches are prominent sites for island nucleation and consequently for the formation of mounds. Also step meandering leads to a non-uniform terrace width. In an in-phase meander the terrace width becomes locally smaller than the initial terrace width $\ell$ [16], but at sites where the phase-shift between consecutive steps is large, large terraces are formed. This is discussed in more detail in the following section. In growth experiments on Cu(1 1 12) a fairly regular array of mounds was observed [5]. This suggests that the mounds do not form independently of each other.

**Vacancies and craters.** – The formation of vacancy islands was studied using kinetic Monte-Carlo simulations of a standard SOS model on a square lattice. The elementary processes are the deposition of atoms at rate $F$ and the hopping of adatoms to nearest neighbor sites with a rate $\nu = \nu_0 \exp(-E_a/k_B T)$. The activation energy $E_a$ includes an energy barrier $E_S$ for diffusion on a flat terrace, a contribution $E_{nn}$ for each lateral in-plane bond, an additional energy barrier $E_{BB}$ for breaking a bond, and an ES-barrier $E_{ES}$, which is implemented through the change in the number of next-nearest neighbors in the planes above and below the hopping atom. The bond breaking barrier $E_{BB}$ serves to enhance step edge diffusion compared to detachment from the step. We used rectangular lattices with $L_x$ ($L_y$) sites along (perpendicular to) the steps and periodic boundary conditions in the $x$-direction. The nominal step spacing was $\ell = 10$. For a detailed description of the model we refer to [16].

The activation barriers were set to the values $E_S = 0.35$ eV, $E_{nn} = 0.15$ eV, $E_{BB} = 0.2$ eV and $E_{ES} = 0.2$ eV. The temperature was $T = 400$ K and the diffusion pre-factor $\nu_0 = 4.17 \times 10^{12}$ s$^{-1}$. For this choice of parameters the steps undergo a meandering instabil-
Fig. 2 – Evolution of the surface morphology after the appearance of vacancy islands. Step pinning leads to the formation of deep craters. After deposition of 40 ML islands form on terraces which are severely deformed due to the neighboring craters. The flux is $F = 2.0\text{ML/s}$ and the system size $200 \times 200$. 

...due to the Kink-Ehrlich-Schwoebel effect (KESE) [10, 16], leading to wavy steps with a wavelength 

$$\lambda_M \approx (12D_s/F\ell)^{1/4}.$$  

(3)

where $D_s$ is the diffusion rate along a straight step; within our model, the activation energy for edge diffusion is $E_S + E_{nn}$. In the KESE instability the steps start to meander with random phase shifts, in contrast to the Bales-Zangwill instability, where the steps meander collectively and the step modulations are in-phase from the outset [16]. Due to the ES barrier the phase correlation increases during time(1), as the steps have a tendency to follow the leading step [19]. Even if the phase correlation increases locally, however, globally the steps remain incoherent, leading to occasional large phase shifts between subsequent steps where two domains of (relatively) coherent meander are joined, see Fig. 1. At these sites the strong meander easily leads to formation of a closed step loop, as a step crosses itself. This process is shown in Fig. 1. For the parameters used in the simulations the critical length $\ell_c \approx 320$, so the formation of mounds due to island nucleation can safely be disregarded. The average distance of islands in the step direction is $\ell_D \approx 100$ even for the largest value used for the flux $F$. In the simulations adatom islands were never observed.

(1)The step meander approaches the in-phase mode even without an ES-barrier, but the ordering process is much slower and the meander wavelength seems to increase during ordering [18].
Fig. 3 – Probability for the formation of a vacancy island in a small system. Results are obtained from 20 independent runs with a deposition flux $F = 5.0 \text{ML/s}$.

Fig. 4 – Mean waiting time $\langle \tau \rangle$ before a vacancy is created for $L_y = 100$ and varying $L_x$, obtained from 20 independent runs for each point with $F = 5.0 \text{ML/s}$. Dashed line shows the expected scaling $\langle \tau \rangle \sim L_x^{-1}$.

Unless the vacancy island created through the self-crossing of a step is rapidly filled, it acts as a pinning center for the following steps. Consequently the pinned steps then also form closed loops around the pinning center, and a deepening crater appears. The development is seen in the snap shots in Fig. 2. It should be noted that the filling of vacancies is severely hampered by the ES-barrier. During further growth, the uphill surface current induced by the ES-barrier [2,3] leads to the deepening, lateral growth and coalescence of craters. As seen in Fig. 2 the ripple pattern is now severely distorted and large terraces between neighboring carters appear. Eventually islands are nucleated on these large terraces, launching the formation of a mound.

Creation of mounds has been observed also earlier in simulations of a similar SOS model [4,7]. In the previous works the meandering of the steps was due to the BZ-instability, rather than the KESE mechanism which is relevant for this work. Also in the earlier works the mounds were seen form preferentially at the sites where the phase coherence between the steps is poor [4, 7].

Statistics of vacancy formation. – We have seen above that the formation of a vacancy island requires a large amplitude meander and a large phase shift between consecutive steps. However, as the meander amplitude grows in time, the phase correlation also improves. The spatial distribution of the vacancies results from the competition between these two effects. To acquire good statistics for the vacancy separation, simulations of extremely large system sizes would be necessary. Here we focus instead on the statistics of the appearance of the first vacancy island in the system.

Vacancy islands were identified as closed step loops in the SOS configuration. This method does not differentiate between vacancy and adatom islands, but in the parameter regime of our simulations no island nucleation takes place on the terraces. The loops were searched by first finding the contour lines separating the lattice in parts where the surface height $h(i, j)$ is higher or lower than some reference height $h_{ref}$. By varying the reference height $h_{ref}$ between the highest and the lowest value of the height in the configuration, all steps are found. After
Fig. 5 – Mean waiting time $\langle \tau \rangle$ for the creation of a vacancy island as a function of the deposition flux $F$ and the bond energy $E_{nn}$. The results are obtained from 20 independent runs for each point. The dashed lines are $\langle \tau \rangle \sim F^{-3/2}$ (left panel) and $\langle \tau \rangle \sim \exp(-E_{nn}/2k_BT)$ (right panel). A slightly different set of parameters was used; the Schwoebel barrier was $E_{ES} = 0.15$ eV, temperature $T = 375$ K and the deposition flux $F = 1.0$ ML/s (right panel). Also the diffusion pre-factor had a different value $v_0 = 1 \times 10^{12}$ s$^{-1}$, so that the ratio $D/F$ remained almost the same.

Finding a step it was checked whether the same point appears in the contour twice, indicating a closed loop. Steps having length 4 were neglected as they mark adatoms.

To study the vacancy separation in the direction of the vicinality it was investigated whether vacancies form at all in systems containing a relatively small number of steps, $L_y/\ell = 4 - 15$. For small $L_y$ the phase coherence propagates through the whole system before the meander amplitude becomes large enough for loop formation and the final configuration is a perfect in-phase step train. For larger $L_y$ vacancies may form before the meander phases have synchronized. Thus varying the system size $L_y$, keeping the step distance fixed, an estimate for the distance between the vacancies in the vicinal direction is obtained. Results from such simulations are shown in Fig. 3. The probability for the creation of a vacancy changes quite rapidly from zero to one as the number of steps in the system increases. The data also show a weak dependence on the step length $L_x$, which we however expect to saturate at large $L_x$.

Based on Fig. 3 we estimate that the distance between vacancies in the $y$-direction is of the order of 50 under the conditions of the simulations.

The most natural candidate for the vacancy distance in the step direction is the meander wavelength $\lambda_M$. To study this length scale, the average waiting time $\langle \tau \rangle$ before the appearance of the first vacancy, starting with a train of perfectly straight steps, was measured. The waiting time is inversely proportional to the number $N_{vac}$ of potential vacancy formation sites. For fixed $L_y$ we expect that $N_{vac} \sim L_x/\lambda_M$, and hence $\langle \tau \rangle \sim \lambda_M/L_x$. Figure 4 confirms that $\langle \tau \rangle \sim L_x^{-1}$, showing that there is a constant vacancy formation probability per unit step length. To test the relation $\langle \tau \rangle \sim \lambda_M$, we have conducted simulations with various values of the growth flux $F$ and the bond energy $E_{nn}$, which control the meander wavelength [16]. Results for $L_x = 200$, $L_y = 100$ are plotted in Fig. 4. Surprisingly, the data are consistent with the relationship $\langle F\tau \rangle \sim \lambda_M^{-2}$, which indicates that the number of potential vacancy sites scales as $\lambda_M^{-2}$ rather than as $\lambda_M^{-1}$. We have no explanation to offer at present. Qualitatively, we note that the deposition flux and the bond energy also affect the growth rate of the meander amplitude and the ordering time scale into the in-phase mode, and hence changing these parameters alters also the vacancy separation in the vicinal direction in addition to the meander wavelength.
Conclusions and outlook. – In this paper we have studied two mechanisms for the destabilization of step flow growth in the presence of an Ehrlich-Schwoebel effect. We have derived a quantitative criterion for destabilization due to mound formation, and presented extensive simulation results for destabilization due to vacancy island formation mediated by strong step meandering. In the latter case we have found evidence for the appearance of a new length scale, proportional to the square of the meander wavelength, which determines the distance between vacancy islands along the step direction.

An important insight is that the vacancy formation process is controlled by the competition between the growth of the meander amplitude and the increase of phase correlations between consecutive steps. This suggests that the behavior may be rather different when step meandering is driven by the Bales-Zangwill-instability, rather than by the KESE mechanism considered here, because in the former case phase correlations are present from the very outset. It may also be of interest to extend the present study to systems without an explicit ES-barrier. On the one hand, in such a system the phase correlations develop much more slowly [18], favoring the formation of vacancy islands; on the other hand, in the absence of the ES-barrier the deepening and coarsening of craters would also be slowed down.

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We are grateful to H.J. Ernst, M. Kotrla, T. Maroutian and O. Pierre-Louis for discussions and correspondence. This work was supported in part by DFG within SFB 237 Unordnung und grosse Fluktuationen, and by Volkswagenstiftung.

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